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**A CHRONOLOGICAL HISTORY OF THE DEVELOPMENT OF
HIGH TEMPERATURE OXIDATION-CORROSION EVALUATION
METHODS INCLUDING AN IMPROVED MICRO OXIDATION-
CORROSION PROCEDURE FOR THE INVESTIGATION OF
ADVANCED GAS TURBINE LUBRICANTS**

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FOREWORD

This report was prepared by the Fluid and Lubricant Materials Branch, Nonmetallic Materials Division, AF Materials Laboratory, Research and Technology Division. Work was initiated under Project No. 7343, "Aerospace Lubricants", Task No. 734303, "Liquid Lubricants Development", with Frank J. Harsacky and Roland E. Dolle acting as project engineers.

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ABSTRACT

An improved micro oxidation-corrosion test method for the effective screening of candidate advanced gas turbine engine lubricants is presented. A method for the preparation of formulations (base fluid plus additives) is also discussed.

Micro oxidation (without metals) and oxidation-corrosion (with metals) evaluation data were obtained for various fluids and compared with results at other laboratories incorporating different test methods.

A brief description of several large scale oxidation-corrosion test methods and a miniature scale oxidation test method developed previously at various laboratories is given.

This technical documentary report has been reviewed and is approved.



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INTRODUCTION

The Air Force Materials Laboratory has been engaged in the synthesis, development and evaluation of high temperature gas turbine lubricants for many years. The Fluid and Lubricant Materials Branch (MANL) was responsible for the development of the current MIL-L-9236 trimethylolpropane (TMP) ester formulations. These anti-oxidant fortified ester fluids were developed to replace the old petroleum base oils and MIL-L-7808 synthetic esters which did not have adequate capability in advanced gas turbine engines above 300°F bulk oil temperature (Reference 1). The TMP ester formulations are currently being evaluated in engine tests for operation at bulk oil temperatures up to 425°F and are subjected to 500°F bearing temperatures.

The more advanced gas turbine engines of the future having Mach 3-4 capability will require lubricants for bulk oil temperatures up to 700°F or higher. Intermittently, these lubricants may encounter hot spots approaching 1000°F.

Essentially, a successful gas turbine lubricant must be capable of withstanding extremely high temperatures in an oxidizing atmosphere (air) for long periods of time as well as possessing good thermal and fluid characteristics. Thus oxidative stability is important toward the selection of a lubricating material for gas turbine engine application.

Since candidate fluids with potentially high oxidative stability are to be characterized, an adequate evaluation method must exist to simulate the severe oxidative environment which will be encountered in operational systems. Also only minimum experimental quantities of new fluids will be available for preliminary evaluation because of the expense involved in their preparation.

When an experimental sample of a candidate gas turbine oil is received by MANL the oxidation-corrosion (O-C) screening test is one of the first evaluations performed. Naturally this initial screening test gives but a broad indication of the oxidative characteristics of a material. It is emphasized that fluids which fail the O-C tests are not rejected or excluded from further study. Based on the overall physical and chemical characteristics of the candidates they may be recommended for other applications such as hydraulic fluid, dielectric coolant, grease base fluid, gear oil, instrument oil, et cetera. Those fluids which demonstrate moderate to good oxidative resistance are evaluated further as gas turbine lubricants, including the preparation of formulations if still better oxidation stability or antiwear characteristics are needed.

Previously, several types of O-C screening tests have been used by MANL. Other types have been employed by industry utilizing different test conditions and varying equipment. Nevertheless, many of the tests are basically similar as they provide a means of comparing classes of materials within a given laboratory.

Federal Test Method Standard No. 791, Method 5308.4, "Corrosiveness and Oxidation Stability of Light Oils (Metal Strip)", was used by MANL and industry for evaluating MIL-L-7808 type synthetic esters to determine their tendency to corrode various metals in an oxidizing atmosphere. The test consisted of immersing five different metal squares in a single glass vessel charged with 100 milliliters of oil at 347°F for 72 hours while agitating the oil with air (5 ± 0.5 liters/hour). A reflux condenser fitted at the top of the oxidation tube was used. The metal squares employed were mild steel, copper, aluminum alloy, magnesium alloy and cadmium-plated steel. Figure 1 illustrates the type of apparatus used and the dimensions. Upon completion of the test, the neutralization number change, percent viscosity change (normally at 100°F), percent fluid evaporation loss, fluid appearance, weight change, and appearance of the metal specimens were determined.

In 1955 an O-C test was introduced (Reference 2) by MANL which utilized a twenty milliliter test sample. One liter per hour of air was bubbled through the sample which contained five washers representing different metals. The metals most commonly used were magnesium, aluminum, copper, silver and mild steel. A reflux condenser was employed. The apparatus is illustrated in Figure 2.

The test method was designed to evaluate the O-C characteristics of petroleum, petroleum products, and related materials at various temperatures. Actually the test was similar to the Federal Test Method Standard No. 791, Method 5308.4 for hydraulic oils except on a smaller scale (one-fifth). Among other similarities the same ratio of air flow to sample size was used. It was believed that this O-C test was not severe enough to adequately evaluate advanced gas turbine fluids.

In 1960 a large scale O-C test was developed at MANL in cooperation with the Celanese Chemical Corporation (Reference 3) specifically for evaluating MIL-L-9236 type fluids at 425°F+. This bench scale method was developed in an attempt to simulate bearing rig and jet engine conditions. Essentially the apparatus (Figure 3) is similar to that used in Federal Test Standard No. 791, Method 5308.4 except for the following modifications:

1. Oxidation tube shortened and elimination of reflux condenser
2. Increased sample size (250 ml)
3. Use of an air flow rate that closely corresponds to that used under operational conditions (to be determined)
4. Elimination of all types of metal specimens except mild steel
5. Samples taken at intermittent periods for viscosity and neutralization number determinations
6. Addition of fresh fluid at intervals to replace evaporation losses

The operating temperature of the bench scale test was adjusted to correspond with the bulk oil temperature encountered in an advanced test rig. As a result of the brief study an air flow rate between 36 and 48 liters per hour through a 250 milliliter sample of an ester fluid gave good correlation with bearing rig data for the same ester (Reference 3). It should be understood, however, that the comparative MANL bench scale and bearing rig data resulting from the short study were obtained for one ester fluid only. Identical test conditions may not be valid for other fluids.

Prior to the development of the MANL bench scale test the Celanese Chemical Corporation developed a similar large scale O-C test which has been described in detail (Reference 3). The test was run for a total of 35 hours in 5-hour test cycles. An aluminum heating block maintained at the desired temperature (normally 425°F) was used as a heat source and 96 liters per hour of dried air were passed through 250 milliliters of test fluid. Five metal squares (copper, mild steel, aluminum alloy, titanium alloy and silver) were immersed in the fluid. No condenser was used at the top of the sample tube. At the end of each 5-hour test cycle, except the last, fresh sample was added to the test tube to make up for the overhead losses. Upon completion of all test cycles except the first and second (5 and 10 hours total test time, respectively) a 20 milliliter aliquot of test fluid was removed for 100°F viscosity and neutralization number determinations. However, the weight of the 20 milliliter aliquot was not "made-up"; only fresh fluid quantitatively equal to the overhead losses was added. At the end of the seventh 5-hour cycle (completion of test) the weight changes and appearance of the metal squares were recorded. Also the neutralization number of the bulk overhead condensate was taken. The basic glassware used for the test is shown in Figure 4.

The principal objection to the Celanese and MANL bench scale tests was the large sample size required (250 ml). As mentioned before, many new fluid candidates are difficult and costly to prepare and often are not available in large quantity.

Under Air Force contract* aimed at the synthesis and evaluation of pyrazine derivatives for use as high temperature stable functional fluids, the Wyandotte Chemicals Corporation developed a miniature scale rapid oxidation screening test (no metal specimens used). A study of the influence of a number of significant variables such as time, air flow rate, air tube orifice size, temperature and sample tube configuration was done to establish the most favorable combination of conditions. A complete description of the investigation has been reported (References 4 and 5).

As a result of the Wyandotte study a set of oxidative conditions were adopted for a moderate and a severe test. The conditions for the moderate oxidation test (no metals used) were 2.0 milliliter sample size, 2.0 millimeter air tube orifice size, 0.5 liters per hour air flow rate, 500°F test temperature and 6 hour duration. The severe test conditions differed only in the use of 2.0 liters per hour air flow with all other conditions the same as the moderate test. The tests were performed at 500°F since this was the bulk fluid temperature under consideration for a fluid arising from the contractual effort. The extent of oxidation was determined by recording the weight loss of the fluid, color change, viscosity change at 100°F and change in the infrared spectrum of the sample. The basic glass apparatus used is illustrated in Figure 5.

A disadvantage of the Wyandotte test was the extremely small sample size. The accuracy of the test may have been compromised and if an appreciable fluid loss was encountered there was not enough fluid remaining for adequate viscosity and neutralization number determinations. Another significant disadvantage to the miniature test was that no metal specimens (O-C effect) could conveniently be used due to the size of the sample tube. Nevertheless, the test methods (both moderate and severe) provided an adequate preliminary screening tool for the purpose of the contractual effort.

*Contract AF 33(616)-6749, monitored by the Nonmetallic Materials Division, Fluid and Lubricant Materials Branch.

For several years the Air Force has been supporting a program* at the Southwest Research Institute (SwRI) concerning the development of lubricant screening tests and evaluation of lubricants for gas turbine engines. One of the objectives of the work was to develop apparatus and procedures for determining the O-C characteristics of high temperature gas turbine lubricants (supplied by the Air Force) under environmental conditions representative of Mach 3 class gas turbine engines.

Two types of O-C tests were developed during the contractual effort. One test was designed primarily for evaluation at 425-500°F and the other for work at 500°F and above. The former test, in which a liquid bath was used as a heating media, was developed in connection with screening MIL-L-9236 lubricants. The latter test utilized an aluminum block as a heat source to extend the temperature capability beyond 500°F.

Early in the contractual program a series of 20 lubricants were evaluated at 425°F using the liquid bath media. Twelve of these lubricants had been previously engine tested at 425°F by the Air Force. According to SwRI good correlation between the O-C test and the engine test was shown (Reference 6). The glassware used in the 425-500°F O-C test was the same as that used by Celanese (Figure 4). A detailed description of the complete apparatus has been reported (References 3 and 6).

Although the SwRI 425-500°F glass test apparatus was identical to the Celanese bench scale test apparatus, the test conditions differed considerably. Briefly, a 350 milliliter fluid sample was charged to the test tube containing five metal squares. The types of metals used were aluminum alloy, silver, titanium alloy, mild steel and stainless steel (the Celanese test used copper instead of stainless steel). The thermostated oil bath was maintained at a specified temperature between 425-500°F. Clean, dried air was bubbled continuously through the lubricant sample at a rate of 197 liters per hour for 18 hours. During the test, condensed oil and vapors are not returned to the sample tube, but are directed to a separate collection system. After the test 100°F viscosity and neutralization number determinations were made and the weight changes of the metal specimens noted. The overhead condensate collected was weighed and evaluated for neutralization number.

The apparatus for the SwRI O-C test at 500°F and above (Figure 6) had the same general configuration as the 425-500°F test except for the following major modifications:

1. A high temperature (700°F+) aluminum heating block was used in place of the liquid bath.
2. The dimensions of the sample tube were altered somewhat to conform to the requirements of the block bath.
3. A glass joint was added to the test tube head for removal of oil samples and oil temperature measurements in overboard tests.
4. A different air delivery tube design was introduced.
5. Round washer type metal specimens were substituted for metal squares.

A standard test procedure incorporating a specific set of conditions for the 500°F+ test has not been completely developed by SwRI. However, an evaluation of existing correlation

*Monitored by the Air Force Aero Propulsion Laboratory, Research & Technology Division.

between the high temperature O-C test and bearing rig test results generally showed excellent agreement of data at 600°F according to SwRI (Reference 7).

Initial 500°F+ O-C work at SwRI involved the evaluation of fluids (principally polyphenylethers) over a wide range of test conditions. Normally the sample size was 200 milliliters (250 ml if excessive volatilization was expected) with a test duration of usually 48 hours. The overboard condensate was not allowed to return to the sample tube. The metal specimens (washers) were the same type used in the 425-500°F O-C test. The air flow rate was varied extensively to determine the influence of that variable in the new test. As usual the bulk property changes of the test fluid and any overhead condensate collected were recorded together with the corrosive effect on the metals.

Again as in the case of the other bench scale tests described, the primary objection to both SwRI O-C tests was the large sample size required.

An improved micro O-C test was developed during this report period involving new methods and equipment design. Some of the good attributes of the other tests discussed above were incorporated in the test.

At least a 20 milliliter sample size was required to obtain the physical property measurements needed after the test. Since it was believed that a high air flow rate was necessary to approach actual gas turbine engine operating conditions a 20 liter per hour air rate was chosen initially. Although this flow rate was substantially severe it proved satisfactory for evaluating most fluids.

A reflux condenser at the top of the sample tube was not used in the improved micro O-C test. An overboard type test was believed more appropriate for simulating actual engine conditions. However an alternate apparatus was developed which would allow for the collection of overboard distillate while maintaining an essentially non-reflux type test. The two sets of test apparatus are illustrated in Figure 7, together with a unique air entry tube design. In addition a new system for the continuous delivery of ultra-dry air was incorporated into the test procedure (Appendix).

The improved micro O-C test is discussed in detail in this report. The apparatus and techniques involved are explained thoroughly and comparative data between the test and the test methods of other laboratories are treated.

DISCUSSION

GENERAL

The improved micro O-C test was developed primarily as a screening tool for evaluating potential gas turbine engine oils. The test procedure and apparatus are described in detail in the Appendix. A method for the small scale preparation of formulations (base fluid with additive(s)) is included. The glass test equipment for the O-C test is illustrated in Figure 7.

The air used for the improved O-C test is supplied by a new air compressor-dryer system (see the Appendix) which is capable of delivering oil free, dry air having a maximum of one part per million of moisture. In previous work (Reference 8) the air used for the micro test contained some moisture (up to 0.3 mol % by spectrographic analysis).

Accordingly a strictly oxidative test was not accomplished; instead, another variable, hydrolytic stability, was introduced. Although the air used for the improved micro O-C test is oil and moisture free for the effect of a purely oxidative atmosphere, it can be saturated with water if necessary for better correlation with certain advanced rig operations.

A new air entry tube (Figure 7) is used which is essentially a length of standard 6 millimeter OD Pyrex glass tubing fabricated at one end with a short 2.0 millimeter ID capillary and a glass button for retaining metal test washers. A glass loop extending several millimeters beyond the capillary orifice allows the air tube to be lifted a standard distance from the bottom of the test tube without the aid of clamps, tape, et cetera. The glass loop is shaped approximately to the contour of the bottom of the test tube; thereby, allowing the air tube to remain centered throughout the test.

The overboard distillate from the micro O-C tests performed during the program were not examined. However, a modified distilling receiver is described (Appendix, Figure 7). With this unique apparatus (topped with a reflux condenser) distillate samples can be collected while maintaining an overboard type test (no refluxing back into test tube). The vapors are carried up the oxidation tube, through the modified distilling receiver and into the condenser. The condensed vapor is collected in the receiver tube rather than refluxed back into the oxidation test tube. The receiver tube has a stopcock for intermittent removal of sample. The condenser can be topped with a line leading to a dry ice trap for collection of more volatile components.

The improved micro O-C test involves passing 20 liters per hour of dry air (<1 ppm moisture) through a 20 milliliter fluid sample containing five metal washers (normally silver, aluminum alloy, titanium alloy, M-10 tool steel and 301 stainless steel) for 24 hours at a desired temperature (up to 800°F) in an aluminum block bath. The overboard condensate is not returned to the sample tube, but is either allowed to pass into an open beaker or collected quantitatively in a modified distilling receiver and dry ice trap. It is emphasized again that the modified distilling receiver for catching the overboard distillate was not used in the tests discussed during this report period. For the purpose of the investigation the volatile products were not examined; thus, a quantitative collection was unnecessary.

During the early development stages of the test, several fluids which had previously undergone bearing rig or engine tests were evaluated using the improved micro O-C conditions to check the validity of the test. Later micro O-C data obtained at MANL for various classes of fluids were compared with laboratory screening test data for the same fluids at SwRI, Wyandotte and the Phoenix Chemical Laboratory. The data obtained from these studies are treated in this report.

The base fluids and formulations examined were obtained from Air Force sponsored in-house and contractual programs or from other industrial sources. When the fluids were proprietary only general class names were given to identify them. All fluids regardless of classification were given Air Force Materials Laboratory identification numbers designated by the prefix ELO.

EFFECT OF IMPROVED MICRO O-C TEST ON STANDARD FLUIDS

The polyphenylether base fluid, m-bis(m-phenoxyphenoxy) benzene (5P-4E, mostly meta isomer) (ELO-62-29)* was selected for checking the severity of the micro O-C test conditions at 500 and 600°F. A trimethylolpropane (TMP) ester of heptanoic acid (ELO-62-27)** and another TMP ester mixture of valeric and pelargonic acids (ELO-62-134)*** both formulated with 1.0 weight percent phenyl α -naphthylamine (PANA) and 1.0 weight percent 5-ethyl-5, 10-dihydro-10, 10-diphenylphenazasiline (5-10-10) were evaluated at 425°F under the new test conditions. At one time or another all three fluid types had been evaluated in a bearing rig. In fact, similar TMP ester formulations which are MIL-L-9236 type were used in actual engine tests. Thus a general knowledge of how the micro test conditions compare with advanced test rig environment could be gained. Table 1 gives the data obtained for the fluids in the improved micro O-C test.

The 5P-4E polyphenylether had low viscosity changes and no neutralization number increases after both the 500 and 600°F tests. The metal specimens were not harmed at either test temperature. Essentially the ether oxidized little and the losses due to volatilization were small even at 600°F. It is apparent that although an overboard type test was used, enough condensing occurred in the upper part of the sample tube to eliminate serious volatilization. (The temperature at various depths within an empty sample tube with and without air flow is shown in the test procedure in the Appendix). Actually some condensation in the sample tube seems justifiable since undoubtedly a certain degree of condensation occurs in the bearing rig and gas turbine engine.

The micro test data for the 5P-4E at 600°F compares favorably with actual bearing rig data at SwRI (Reference 6). In fact the viscosity change at 100°F (12.4%) for the ether type**** after 24 hours in a bearing rig (600°F sump oil temperature, 650°F bearing temperature, 1 cfm air flow to oil sump) was almost identical to the 600°F micro test results.

The ELO-62-134 TMP ester formulation withstood the severe micro O-C conditions well at 425°F. A low viscosity change and small neutralization number increase were recorded. None of the metals were seriously damaged, no insoluble formation occurred and the fluid loss was unusually low. Generally the 425°F data compares well with previous data recorded for engine tests at the same temperature for that type of ester formulation***** (Reference 6).

A sharp contrast is observed in the 425°F micro test results for the ELO-62-27 TMP ester formulation. A large viscosity and neutralization number change was recorded. The silver specimen had a significant weight loss, while the other metals essentially did not change. The fluid loss for the ester formulation was high compared to that for the

* Obtained from the Monsanto Chemical Company

** Base Stock 704, Lot 1019, obtained from the Celanese Chemical Corporation

*** Pentalube TP-653, Lot 261G, obtained from the Heyden Newport Chemical Corporation

**** A 5P-4E polyphenylether (mostly meta isomer) designated as F-1041 at SwRI.

***** Basically the same as the ELO-62-134 formulation, but a different base fluid lot.

ELO-62-134 ester formulation under identical test conditions. Advanced engine tests on the same type of formulation* at 425°F resulted in considerably lower bulk property changes (Reference 6). The reason for the unusually poor behavior of the ELO-62-27 formulation in the micro test is not fully understood; however, further discussion of this material will be achieved later.

As a result of the preliminary evaluations using the 20 liters per hour air flow rate, it was concluded that generally the micro O-C test was comparative with advanced test rigs in its treatment of the 5P-4E polyphenylether base fluid and the ELO-62-134 TMP ester formulation. Only in the case of the ELO-62-27 ester formulation did the micro test conditions appear too severe.

Thus it was decided that the 5P-4E neat fluid and the ELO-62-134 ester formulation would be used as standards for comparing the oxidative performance of new candidate gas turbine oils in the 500-600°F and 425°F range, respectively.

IMPROVED MICRO O-C TEST VERSUS SwRI BENCH SCALE O-C TEST

Three ester formulations which had been evaluated at SwRI in the 425-500°F bench scale O-C test (Reference 6) were subjected to the MANL improved micro O-C test at the same temperatures. The results at both laboratories were compared, together with data obtained at 600°F for 5P-4E polyphenylether**.

It will be recalled that the SwRI 425-500°F test involves passing 196 liters per hour of dried air through 350 milliliters of test sample for 18 hours. The overboard condensate is not returned to the sample tube and a liquid heating bath is used. The SwRI 600°F tests using the 5P-4E were carried out in an aluminum block bath and 130 liters per hour of dried air was passed through a 250 ml test sample. The 5P-4E was tested by SwRI for various periods of time (Reference 9), but only the results after the 24 hour test were compared with the MANL micro test.

The same type of metals were used in the O-C tests at both laboratories except SwRI used a mild steel specimen instead of tool steel.

It was considered important to compare the improved micro test with the SwRI tests because most all candidate gas turbine fluids submitted to the Air Force Aero Propulsion Laboratory are first screened via a series of SwRI bench scale O-C tests at various temperatures. Fluids which pass the O-C evaluation and other preliminary tests satisfactorily are often evaluated in a bearing rig. Usually a one-half to one gallon quantity of fluid is required for the O-C characterization alone. A smaller O-C test (20 ml sample) giving comparable data with the larger test would be advantageous to the supplier of a candidate fluid, especially if it is expensive and difficult to synthesize. Thus an initial large scale synthesis may be avoided if a material should fail to show promise for bearing rig or engine testing. Table 2 summarizes the data obtained at both laboratories for the representative fluids.

* Basically the same as the ELO-62-27 formulation, but a different base fluid lot.

** This material was designated at LRO-13 at SwRI

At 425 and 450°F the resorcinyl dineoheptanoate* formulation (ELO-62-50) had considerably higher bulk property changes after the SwRI tests than in the MANL micro tests; although SwRI utilized a proportionally lower ratio of air flow to sample size. The metal specimens from the tests at both laboratories had nearly the same negligible weight changes.

At 475°F the test results for the diester formulation at both laboratories were closely comparable, with the viscosity change after the SwRI test being slightly lower. Most of the metals from both 475°F tests gained about the same magnitude of weight.

At 500°F the formulated dineoheptanoate degraded badly at both laboratories with the micro test being somewhat more severe. All the metal specimens in both 500°F tests gained weight with the bench scale test generally resulting in larger weight increases.

The reason why the SwRI test resulted in much higher bulk property changes for the resorcinyl diester formulation than the micro test at 425-450°F is not completely understood. It may be that the contrast between the two tests was caused by the differences in temperature in the upper portion of the test tubes (liquid bath versus air bath.) The SwRI test utilizing a liquid heating media would undoubtedly give more uniform and higher temperatures within the immersed portion of the test tube; whereas, the temperatures in the test tube near the top of the aluminum block (air media) are nearly 100°F less than at the bottom (micro O-C procedure in Appendix). The mere fact that the diester fluid loss due to more volatilization was heavy in the 425-450°F SwRI tests would account for an elevated viscosity even though minor degradation may have occurred. Also puzzling is that the SwRI test gave lower bulk property changes for the formulation at 475°F than at 425 and 450°F.

The fact that the ELO-62-50 diester formulation has previously demonstrated peculiar volatility characteristics (Reference 8) may be another answer to the anomaly existing between the two test methods.

It is believed that the micro test gave more indicative results; that is, the bulk property changes recorded after the micro test illustrated actual degradation of the diester and not change due to volatilization (concentration of high viscosity residues). As the temperature was raised in the MANL micro test the diester's resistance to oxidation decreased which is normally the general stability pattern for most fluids.

The proprietary polyolester formulation (ELO-62-39) data (bulk property changes including fluid evaporation loss) at 450 and 500°F obtained in the MANL micro and SwRI bench scale tests were closely agreeable. The metal weight changes after the 450°F tests were nearly the same at both laboratories. At 500°F the silver and mild steel specimens lost significant weight at SwRI; whereas, no appreciable weight changes occurred in the micro test.

Both laboratory tests can be considered closely comparable in their treatment of the polyolester formulation which showed reasonably good oxidative stability at 500°F which is unusual for ester type fluids.

*Base fluid obtained from the Celanese Chemical Corporation under Air Force Contract No. AF 33(616)-6786.

The micro test involving the polyphenylether resulted in a lower viscosity change for the base fluid than the larger SwRI test. Both tests were conducted for a period of 24 hours. No neutralization number change was found at either laboratory and the metal specimens in the micro test were not harmed (metal specimens were used in the SwRI test but their weight changes were not available in the reference data). Again the bench scale test resulted in an exceptionally large fluid loss for the 5P-4E (60%). Regardless of the large difference in fluid loss in the two tests, the results at both laboratories were considered comparable or of the same magnitude since the 5P-4E did not degrade significantly in either test.

The ELO-62-27 TMP ester formulation degraded considerably more in the 425°F micro tests than in the full scale O-C test; although the SwRI test results showed appreciable degradation as evidenced by a high neutralization number increase (4.7 mg KOH/g) and a substantial viscosity change. In the micro test the silver metal was significantly attacked, but none of the metals in the SwRI test were harmed.

As already shown (Table 1) the ELO-62-134 TMP ester formulation had unusually low bulk property changes after the MANL Micro O-C test at 425°F. In fact the bulk property changes for the formulated ester were generally similar to or lower than those obtained for ELO-62-27 type and other TMP ester formulations at SwRI (Reference 6).

It was not clearly understood why such a contrast in oxidative stability should exist between the ELO-62-27 and ELO-62-134 TMP ester formulations in the MANL tests. To determine the sensitivity of both TMP ester formulations to the conditions of the micro O-C test without varying test duration (24 hours) or temperature (425°F) tests were conducted using 5, 10, 15, 20 and 25 liters per hour air flow rates (ELO-62-134 formulation was tested using 30 liters per hour also). The five standard metal specimens were used for their effect on the oxidation process, but the weight changes were not recorded.

It was believed that the results from such a series of tests might indicate whether a slightly lower air rate would result in considerably lower oxidative deterioration of the ELO-62-27 formulation. In other words, the question of whether the formulation was borderline under the standard micro O-C conditions could be answered. Also the maximum test severity (air flow rate) to be applied in evaluating the formulated ELO-62-134 and still give only slight degradation could be ascertained. The duplicate micro O-C data produced from the above experiments are found in Tables 3 and 4. Curves derived from the data in the tables (viscosity increase versus air flow rate) are shown in Figures 8 and 9.

In the tests utilizing greater than 5 liters per hour air rates the formulated ELO-62-27 ester degraded significantly. The oxidative stability of the formulation during the 25 liters per hour test was extremely poor.

In contrast the formulated ELO-62-134 ester maintained very good oxidative resistance in the tests using up to 25 liters per hour air rate. In fact the viscosity and neutralization number changes for the formulation tested with 5, 10, 15, 20 and 25 liters per hour of air were practically identical. However, at the 30 liters per hour air rate the formulation degraded badly.

Thus the use of the formulated ELO-62-134 TMP ester as a standard for comparing candidate gas turbine fluids at 425°F was justified. The ester formulation more than

withstands the severe conditions of the improved micro O-C test (20 liters per hour air flow rate) without appreciable bulk property changes. This correlates well with data obtained at SwRI on the same type of formulated ester.

The fact that the ELO-62-27 does not appear to possess the same oxidative ability as ELO-62-134 is not completely understood. However, according to SwRI (Reference 6) the ELO-62-27 type formulation was consistently the most critical fluid of the group of esters evaluated and its performance was the limiting factor in the severity of the bench scale test. Investigators at SwRI found that the ester formulation was extremely sensitive to slight variations in temperature ($\pm 5^\circ\text{F}$) during 425°F O-C tests. Thus the temperature deviation of the micro O-C test ($\pm 5^\circ\text{F}$) may be enough to cause a significant difference in the results at MANL and SwRI. Also it should be noted that different lots of the ELO-62-27 type fluid were evaluated at each laboratory.

In view of the interesting results obtained for the TMF ester formulations by varying the air flow rates in the micro O-C tests, the 5P-4E polyphenylether was treated similarly. The air flow was varied up to 35 liters per hour while the test time and temperature were maintained at 24 hours and 600°F , respectively. The data are summarized in Table 5 and Figures 10 and 11.

The highest viscosity increase was recorded after the one liter per hour test and the second highest viscosity after the 5 liters per hour test. The lowest increase in viscosity occurred at 25 liters per hour. Actually, the tests employing 15 to 30 liters per hour air rates gave closely comparable viscosity changes (within 8 centistokes). The 35 liters per hour test resulted in a slight upward trend in viscosity increase again. The fluid losses were relatively low (less than 10%) through the 30 liters per hour test; however, at 35 liters per hour considerable volatilization occurred (38.7%). It is interesting that the viscosity increase for the latter test was less than half that recorded for the one liter per hour experiment which resulted in less than one percent fluid loss. The fluid loss during the 25 liters per hour test was unexpectedly high, greater than after the 30 liters per hour test. No neutralization number increase was found for the ether after any of the experiments.

The unusual effect on the 5P-4E polyphenylether produced by varying the air flow was also encountered at SwRI in their studies with the same material (Reference 6). SwRI believed the phenomenon may be due to vapor-phase oxidation. According to their theory at the low air rates a large portion of the products of vapor-phase oxidation is subject to condensation and runs down the sample tube thereby having an important effect on the bulk oil condition. As the air flow is increased the residence time of the oil vapors is decreased so that vapor-phase oxidation and its effect on the bulk oil is also decreased. At still higher air flow rates the effect of vapor-phase oxidation becomes insignificant; thus, the primary mechanism is deterioration of the bulk oil sample.

As a result of recent work by the Monsanto Research Corporation (Reference 10) a tentative mechanism for the oxidation of polyphenylethers was proposed. It was believed by the Monsanto investigators that hydrogen abstraction to form phenyl radicals occurs first resulting in intramolecular ring closures. At a later stage, oxygenation of the phenyl radicals takes place with subsequent coupling to form higher molecular weight (higher viscosity) compounds. This type of degradation in conjunction with the SwRI theory may be a creditable explanation of the unusual behavior of the 5P-4E polyphenylether toward varying air flow rates in the SwRI and MANL tests.

The data obtained from the MANL micro O-C tests for 5P-4E at various flow rates lend support to the SwRI theory. In the micro experiments the low air rates gave rise to low fluid losses and unusually high viscosity increases, indicating that small concentrations of vapor-phase oxidation products may have enhanced further degradation by condensing and returning to the bulk fluid. At higher air flow rates these harmful products were "swept" out of the test tube. This may have occurred during the 25 liters per hour experiment where the fluid loss was abnormally high and the viscosity increase dropped slightly (Figures 10 and 11). The upward trend in viscosity increase at the 35 liters per hour air rate was attributed to considerable volatilization of unchanged ether resulting in an increased concentration of high molecular weight moieties from vapor-phase decomposition.

The above discussion not only demonstrates the effect of air flow rate on the polyphenyl-ether but also poses some questions as to the profile of advanced lubricant systems from the standpoint of air flow and amount of condensation possible. The 5P-4E would be applicable in a gas turbine engine if the air flow rate in such a system was somewhat more than moderate, which is believed to be the case. However, the performance of the ether may be compromised in a hydraulic system where the concentration of air is small and volatilization minimized.

IMPROVED MICRO OXIDATION TEST VERSUS WYANDOTTE MINIATURE OXIDATION TEST

A series of reference fluids of various classes were evaluated oxidatively by the Wyandotte Chemicals Corporation under Air Force contract* as part of a pyrazine synthesis and evaluation program (Reference 5). The severe miniature test results at Wyandotte were compared with those from the MANL micro test (no metals used). It was important that the tests at both laboratories compare favorably in order that new pyrazine fluids prepared under the program would be screened more effectively prior to MANL evaluation.

As discussed earlier, the severe Wyandotte miniature oxidation test utilized a 2 milliliter sample through which 2.0 liters per hour of dried air was passed for 6 hours. No reflux condenser or metal specimens were used. A 500°F test temperature was chosen since that was the temperature at which a fluid arising from the program must be oxidatively stable. The MANL micro test evaluation of the same fluids was also conducted at 500°F without metal specimens for 6 hours for comparative reasons. The results from both tests are summarized in Table 6.

The Wyandotte test results agreed very well with those obtained at MANL. The fluids that survived the miniature test had good oxidative resistance in the MANL test also as evidenced in the case of the DC-710 silicone, 5P-4E and 2-phenoxy-3-(5-nonyl)pyrazine. The remaining fluids that degraded substantially at Wyandotte did poorly in the MANL micro test. Essentially the oxidative (absence of metals) performance of all the reference fluids in the MANL test could be predicted in advance at Wyandotte with reasonable confidence.

The good correlation between the Wyandotte and MANL tests is a significant advantage in a lubricant synthesis and evaluation program in which many candidate fluids are prepared for screening in less than 5 gram quantity. Only those fluids which are oxidatively

*Contract AF 33(616)-6749, monitored by the Nonmetallic Materials Division, Fluid and Lubricant Materials Branch.

outstanding in the miniature test without metals need be prepared in greater quantity for evaluation in the MANL micro test with metals.

IMPROVED MICRO O-C TEST VERSUS PHOENIX MICRO O-C TEST

A test almost identical to the MANL improved micro O-C test was made operational at the Phoenix Chemical Laboratory under Air Force contract* to provide another source for acquiring micro oxidation-corrosion data on candidate materials. By making their own arrangements with Phoenix, industrial laboratories can obtain preliminary data on their newly developed fluids and submit only the most promising samples to the Air Force for a more complete characterization. Since MANL will accept the data obtained at the Phoenix laboratory, not only is the workload reduced at MANL, but the complete characterization of a particular fluid is expedited. Table 7 shows comparative data for three fluids evaluated at various temperatures in micro O-C tests at Phoenix (Reference 11) and MANL. Results of tests performed without metals present are given also.

The data obtained at both laboratories for each fluid were very similar in all tests. In practically every case the fluid loss, viscosity change, neutralization number change and metal weight changes recorded at the two laboratories were nearly identical within the reasonable limit of error of the tests. Certainly the preliminary micro O-C evaluation data from Phoenix would be accepted by MANL.

CONCLUSIONS

Generally the improved micro O-C test compared favorably with the SwRI large scale test for screening candidate gas turbine lubricants prior to bearing rig characterization. Results from Wyandotte's miniature oxidation test and Phoenix's micro oxidation and micro O-C tests were closely comparable with those from the MANL micro tests.

It is believed that the improved micro O-C test is effective for the oxidative screening of candidate fluids subsequent to bearing rig evaluation without using excessive quantities of experimental fluid needed in the larger scale tests. Still the micro test is large enough that metal washers can be used and the necessary bulk property changes of the fluid obtained after the test.

The use of 5P-4E polyphenylether and the ELO-62-134 TMP ester formulation as standards for comparing the oxidative stability of new candidate gas turbine oils at 500-600°F and 425°F, respectively was established. The micro O-C test results for the two fluids were similar to those obtained from large scale O-C tests and advanced rig characterization.

*Contract AF 33(657)-8771, monitored by the Nonmetallic Materials Division, Fluid and Lubricant Materials Branch.

RECOMMENDATIONS

It is recommended that the improved micro O-C test continue to be used for screening new candidate gas turbine engine oils for subsequent advanced rig characterization.

It is proposed that the micro O-C test be modified further to evaluate hydraulic fluid candidates and other high temperature functional fluids which are not required to have high oxidative stability. Also the development of a combination micro hydrolytic stability and O-C test is suggested using water saturated air which is currently employed in some bearing rig operations.

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APPENDIX I

IMPROVED MANL MICRO OXIDATION-CORROSION TEST PROCEDURE

1. Equipment

a. Pressurizer- Dehydrator System*: An air compressor-dryer unit (Model 100-183 Gilbarco) containing an oilless compressor, automatic heatless dryer, moisture indicator, back pressure regulator, high and low pressure alarm switch, relief valve, two shutoff valves, two pressure gauges, manual on-off switch with pilot light and another back pressure regulator. The heatless dryer included in the system consists of two cylindrical chambers containing desiccant and mounted on a manifold block. Within the manifold are passages-inlet, outlet, purge openings, and a small passage connecting the two chambers. The passages are opened and closed by two three-way solenoid valves. These are operated by a timer driven by a small synchronous electric motor. The operating action of the dryer is alternating in thirty-second cycles. While one chamber is drying, the desiccant in the other is purged of moisture. The dryer-compressor unit is capable of delivering dry air at a continuous steady flow of 120 standard cubic feet per hour (maximum), 0-30 pounds per square inch (gauge) pressure, and one part per million by volume of moisture (maximum).**

b. High Temperature Aluminum Block Bath (Reference 12): The bath consists of two solid cast aluminum blocks fabricated to receive thermocouples and twelve 500 X 22 millimeter micro O-C tubes (original holes for standard 500 X 50 millimeter test tubes are fitted with transite bushings to accommodate the micro tubes). The bath heaters are controlled with a Brown electronic circular scale controller (Range 0-1200°F). The control circuit is actuated by two thermocouples (one in each block) which are connected in parallel. To achieve greater temperature flexibility, a ten-hole and six-hole aluminum block bath of similar construction are also used. The baths can be conveniently operated to a maximum temperature of 800±5°F.

c. Flowmeters: Fischer and Porter Minirators (range 0-40 standard liters per hour) with needle control valve located in the inlet fitting. The flowmeters are mounted in manifold arrangement on a panel board.

d. Centrifuge: Clinical type, equipped with a speed control rheostat. Maximum speed is 3200 RPM. Normal operating speed is 1600 RPM. Fabricated to contain four 40 milliliter glass centrifuge tubes. (115v, AC)

e. Test Tube: Pyrex glass tube, standard wall, 22±1 millimeters inside diameter and 500±5 millimeters long. The upper end is fitted with a female $\frac{24}{40}$ joint. The tube is calibrated and etch-marked for twenty milliliters volume (Figure 7).

* Purchased from Gilbert and Barker Manufacturing Company, Applied Pneumatics Division, West Springfield, Massachusetts.

**The moisture content of the air was measured with a Gilbarco Sorption Hygrometer, a moisture analyzer utilizing a quartz transducer and capable of measuring water vapor in air from <1 to 25,000 ppm.

f. Take-off Adaptor (fitted at top of test tube): Three-way, Pyrex glass connecting tube with a side arm at an angle of 75° from lower joint. The lower end and side arm are equipped with male $\frac{24}{40}$ joints and the upper end with a female $\frac{24}{40}$ joint. The distance between the lower end and upper end is 160 ± 4 millimeters. The side arm is 80 ± 2 millimeters (on center) above the lower end (Figure 7).

g. Modified Distilling Receiver (fitted at top of test tube): Pyrex glass, vapor tube having a male $\frac{24}{40}$ joint at the bottom and a female $\frac{24}{40}$ joint at the top with a side arm at an angle of 75° downward connected to the receiver tube. The distance between the lower end and upper end of the vapor tube is 160 ± 4 millimeters. The side arm is 80 millimeters (on center) above the lower end. The receiver tube (20 ml capacity bulb) has a $\frac{19}{38}$ female joint at the top and a $\frac{1}{2}$ Teflon stopcock plug at the bottom (Figure 7).

h. Air Entry Tube: Pyrex glass, standard wall, 6 millimeters OD, fitted with a short 2.0 millimeters ID Pyrex glass capillary at one end. The capillary is constructed with a Pyrex glass "button" 6 millimeters from the orifice to support metal specimens. A Pyrex glass loop was made to extend 8 millimeters beyond the end of the capillary to raise the orifice off the bottom of the test tube. The total length of the air tube is at least 50 millimeters longer than the combined lengths of the test tube and adaptor (or bulb type condenser if used) (Figure 7).

i. Glass Spacer: Standard wall, Pyrex glass with a diameter (7 mm ID) such that it will slip over the air entry tube and rest between the metal test specimens. The spacer is 6 millimeters long (Figure 7).

j. Metal Test Specimen: Disc, 3/4 inch diameter with a centered 1/4 inch diameter hole and cut approximately 0.032 inch thick. The composition of the five metals most commonly employed are listed below:

Aluminum (2024 type alloy)

0.15% silicon
0.75% manganese
4.68% copper
0.43% iron
1.59% magnesium
Balance Aluminum

Titanium (alloy)

6.0% aluminum
3.6% vanadium
Balance Titanium

Tool Steel (M-10 type)

0.36% silicon
0.28% manganese
0.37% carbon
4.07% chromium
7.89% molybdenum
1.85% vanadium
0.76% tungsten
Balance Iron

Stainless Steel (301 type)

0.48% silicon
1.16% manganese
0.04% carbon
17.21% chromium
7.36% nickel
Balance Iron

The silver metal is of electrolytic grade and is 99.9+ percent pure.

k. Condenser: Graham (spiral type), Pyrex glass, 600 millimeters jacket length with a male $\frac{19}{38}$ joint at the bottom and a female $\frac{19}{38}$ joint at the top.

l. Condenser: Allihn (bulb type), Pyrex glass, 300 millimeters jacket length (6 bulbs) with a male $\frac{24}{40}$ joint at the bottom and a plain outlet tube at the top.

m. Condenser: Allihn (bulb type), Pyrex glass, 200 millimeters jacket length (3 bulbs) with a male $\frac{19}{38}$ joint at the bottom and a female $\frac{19}{38}$ joint at the top.

n. Long Stem Funnel: Pyrex glass, 420 millimeters long stem (8 millimeters ID) of heavy wall tubing. Inside diameter of funnel top is 50 millimeters.

o. Balance: Automatic, capable of weighing up to 800 grams with a 0.05 gram sensitivity.

p. Analytical Balance: Automatic, capable of weighing up to 100 grams with a 0.05 milligram sensitivity.

q. Rubber Stopper: One-hole, neoprene base, oil and high temperature resistant, size No. 5

2. Procedure

The metal test specimens are polished to a smooth finish, rinsed in naphtha solvent, wiped dry, and weighed precisely to 0.1 milligram. The weighed metal specimens are inserted on the air entry tube with glass spacers between each specimen (Figure 1). The order in which the metal specimens are located on the entry tube is as follows:

titanium alloy (top specimen nearest surface of fluid)

aluminum alloy

M-10 tool steel

silver

301 stainless steel (bottom specimen nearest air entry tube orifice)

The air tube holding the specimens is placed in the test tube and the assembly weighed to 0.1 gram, then the air tube and specimens are removed. The test tube is charged with 20 ± 0.5 milliliters (to the 20 milliliter etch mark) of fluid sample. (A long stem funnel may be used to introduce the fluid into the test tube). The air tube and metal specimens are replaced and the tube and contents reweighed. The weight of the fluid added is recorded to the nearest 0.1 gram.

In the "overboard" test (no condenser used) the take-off adaptor is placed directly at the top of the test tube. The air tube is held firmly in place with a 1-hole neoprene rubber stopper at the upper end of the adaptor.

When collection of volatiles is desired a modified distilling receiver topped with a 600 millimeter (jacket length) spiral condenser is used (Figure 7). A dry-ice acetone cold trap may be employed to collect highly volatile components which escape through the condenser.

The air tube is held firmly in place with a neoprene stopper at the top of the vapor tube part of the distilling receiver while the condenser is fitted at the top of the receiver side. Thus an "overboard" type test is maintained, but volatiles are retained in the distilling receiver and cold trap for subsequent analysis.

The test tube assembly is placed in an aluminum block bath preheated to the desired temperature. The test tube is submerged 410 ± 5 millimeters into the bath (only 300 ± 5 mm of the test tube is actually in the aluminum block).

As an illustration, the temperature at various heights within an empty glass micro O-C tube (with and without air flow) placed in the block bath controlled at 425°F is shown below:

Position in O-C Tube, millimeters from bottom of tube	Position Temperature, $^\circ\text{F}$	
	No Air Flow	20 liters/hr Air Flow
0 (Bottom of aluminum block)	424	424
50	424	424
100	423	423
150	420	420
200	413	413
250	393	388
300 (Top of aluminum block)	347	342

A piece of 4×2.5 millimeter amber, gum rubber tubing leading to a calibrated flowmeter is fitted tightly to the top of the air tube. Dry air (<1 ppm moisture) is metered through the air entry tube via the flowmeter at the rate of 20 ± 0.5 liters per hour. The duration of the test is 24 hours from the time the air flow is started.

At the end of 24 hours, the rubber tubing is disconnected from the top of the air entry tube and the test tube assembly is removed from the block bath and allowed to cool at room temperature.

The take-off adaptor (or distilling receiver and condenser if used) is removed and the test tube and contents (air tube, metal specimens, and fluid sample) are weighed to within 0.1 gram. The percent evaporation loss is computed from the original combined weight of the air tube, metal specimens and fluid sample before the test.

The air tube and metal specimens are then removed and the specimens are rinsed (not wiped) in naphtha solvent. The metals are examined for tarnish (discoloration) and or corrosion first, then cleaned with naphtha solvent and wiped dry. The metal specimens are weighed to 0.1 milligram and the weight change of the metals is computed and recorded in milligrams per square centimeter of surface exposed to the oil.

The residual oil in the test tube is examined for insoluble material and appearance. If insolubles are present, the sample is centrifuged and the supernatant fluid is analyzed for neutralization number change* and percent viscosity change at 100°F ** (based on the neutralization number and viscosity of the original, unoxidized fluid sample taken and recorded prior to the test.)

* Federal Test Method Standard No. 791, Federal Test Method 5105.3 using Beckman automatic titrator instead of colorimetric titration.

**Test for Kinematic Viscosity, ASTM Designation: D445-61, using Cannon-Manning semi-micro type viscometers.

The insoluble material remaining in the centrifuge tube is washed three times with naphtha solvent by centrifuging and decanting. The oil free insolubles are dried in an oven and weighed. The weight percent insoluble formation is calculated and recorded based on the weight of the oil sample before the test.*

In summary, the following data are obtained and recorded:

- (1) Percent fluid evaporation loss
- (2) Percent viscosity change at 100°F
- (3) Neutralization number change (mg. KOH/g.)
- (4) Fluid appearance
- (5) Percent insoluble formation
- (6) Weight change (mg/cm²) and appearance (before wiping) of each metal.

IMPROVED MANL MICRO OXIDATION (NO METALS) TEST PROCEDURE

Equipment and procedure same as in the improved MANL micro O-C test, except no metal specimens or glass spacers are used.

*In earlier work (Reference 13) the weight percent insoluble formation was estimated (based on the residual fluid remaining after the test) and only recorded as light (<0.2 wt %), moderate (0.2-2 wt %), heavy (2-5 wt %) or very heavy (>5 wt %).

APPENDIX II

PREPARATION OF FORMULATED FLUIDS FOR EVALUATION IN THE IMPROVED MANL MICRO O-C TEST

1. Equipment

a. Servall Omni-Mixer Homogenizer*: A high speed mixer unit consisting of a support stand, motor (16,000 RPM, max.) mounted on an adjustable sliding bracket, removable stainless steel rotor-knife blade assembly, and a 65 milliliter capacity stainless steel chamber (basic unit is adaptable to capacities from 5 ml to 2000 ml). The mixing chamber is fitted with a custom made electric heating mantle. Inserted between the mantle and chamber is an iron-constantan thermocouple leading to a recorder. Both the mixer motor and heating mantle are controlled with a "variac" transformer (115v).

b. Analytical Balance: Automatic, capable of weighing up to 200 grams with a 0.5 milligram sensitivity.

c. Centrifuge: Industrial type, equipped with a speed control rheostat, (maximum speed is 5100 RPM). Normal operating speed is about two-thirds maximum. The unit is fabricated to contain four 40 milliliter or 100 milliliter glass centrifuge tubes. (230v, AC, single phase)

2. Procedure

The base fluid (normally about 50 ml) is charged to a tared stainless steel mixing chamber and weighed to the nearest milligram. The quantity of additive to be charged is calculated based on the net weight of the base fluid and the desired additive concentration. The additive is then weighed into the mixing chamber to the nearest milligram.

The chamber is attached to the Omni-Mixer unit and allowed to stir with heating under the following suggested conditions:

Mixer "variac" transformer setting, volts	60-80 (max)
Temperature of chamber and contents, °F	180-212 (max)
Total mixing time**, minutes	5

After the mixing process the chamber is removed and the contents allowed to cool slowly to room temperature. If additive precipitation occurs, the sample is transferred to a 100 milliliter glass centrifuge tube and revolved in the centrifuge (3000-3500 RPM) until separation is complete (normally 15-20 minutes). The supernatant fluid is then decanted into a sample bottle and retained for subsequent characterization.

The residual additive in the centrifuge tube is washed free of oil by stirring the precipitate in naphtha solvent followed by centrifuging and decanting (the washing process is repeated twice). The washed precipitate is dried in an oven at normally 210-250°F for several hours and weighed. The percent additive remaining in the base fluid is calculated.

* Manufactured by Ivan Sorvall, Inc., Norwalk, Connecticut.

**Does not include time required for chamber and contents to heat to 180-212°F.

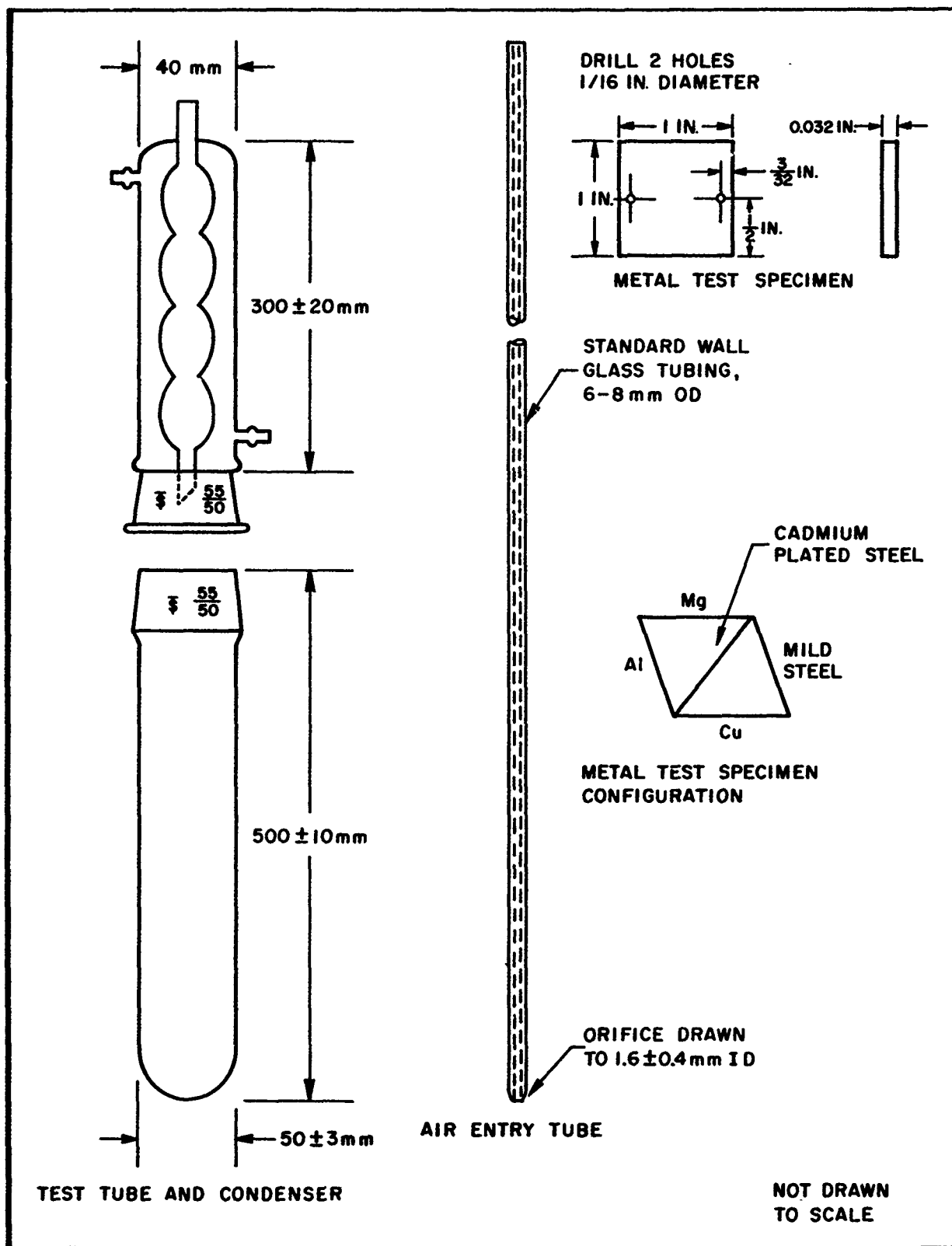


Figure 1. Method 5308.4 O-C Test Apparatus

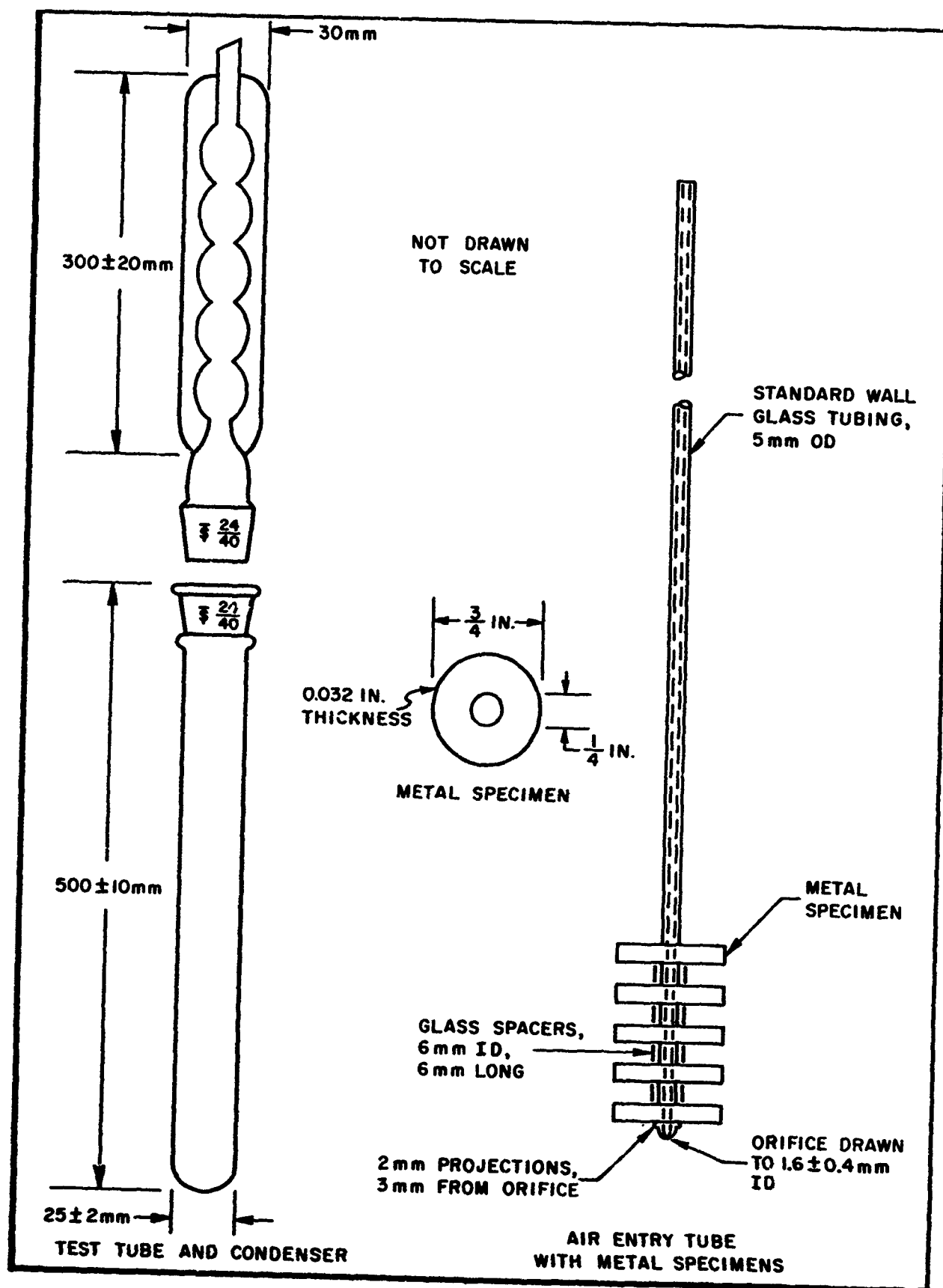


Figure 2. MANL Micro O-C Test Apparatus For Petroleum, Petroleum Products, and Related Materials

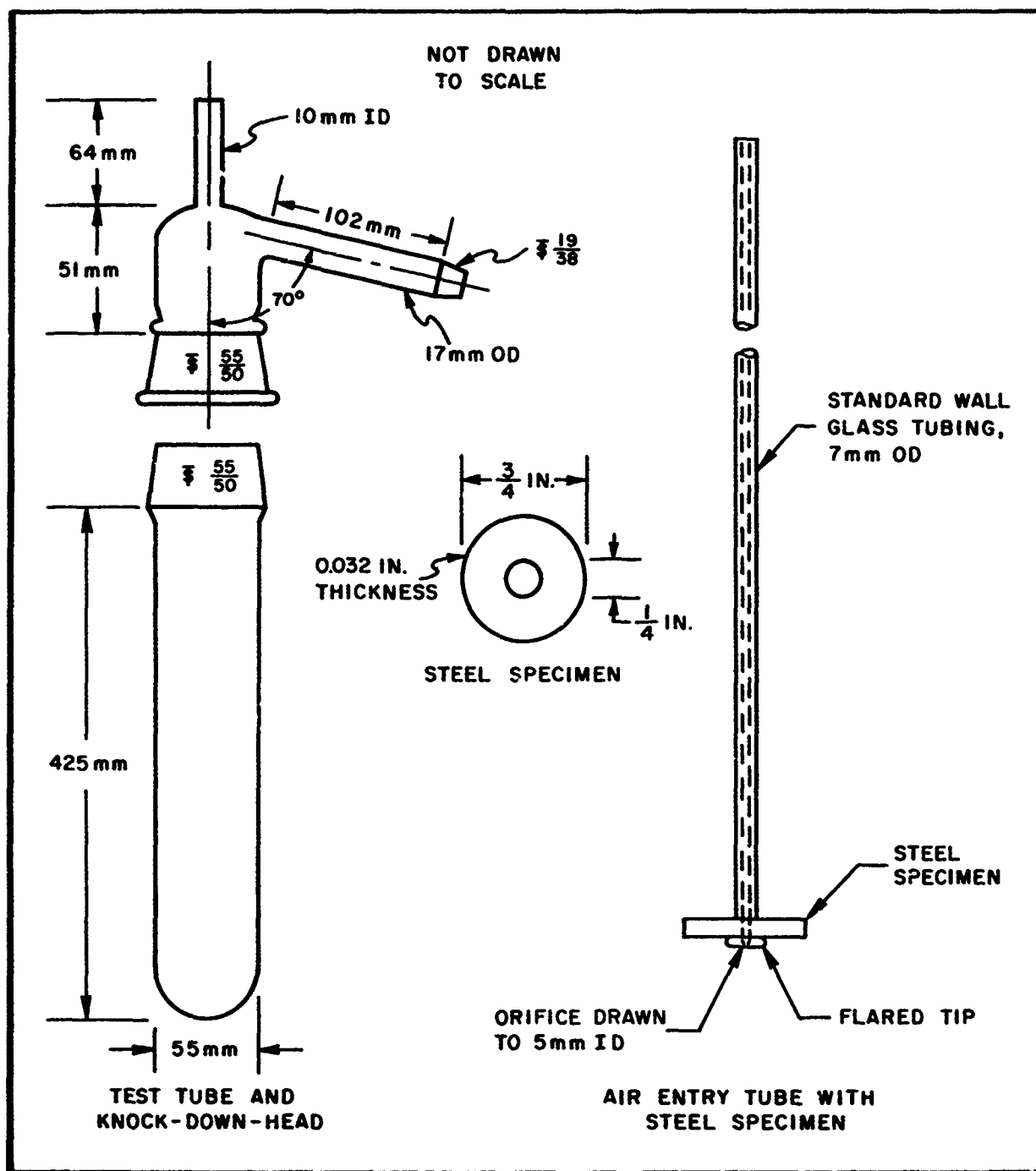


Figure 3. MANL Bench Scale O-C Test Apparatus

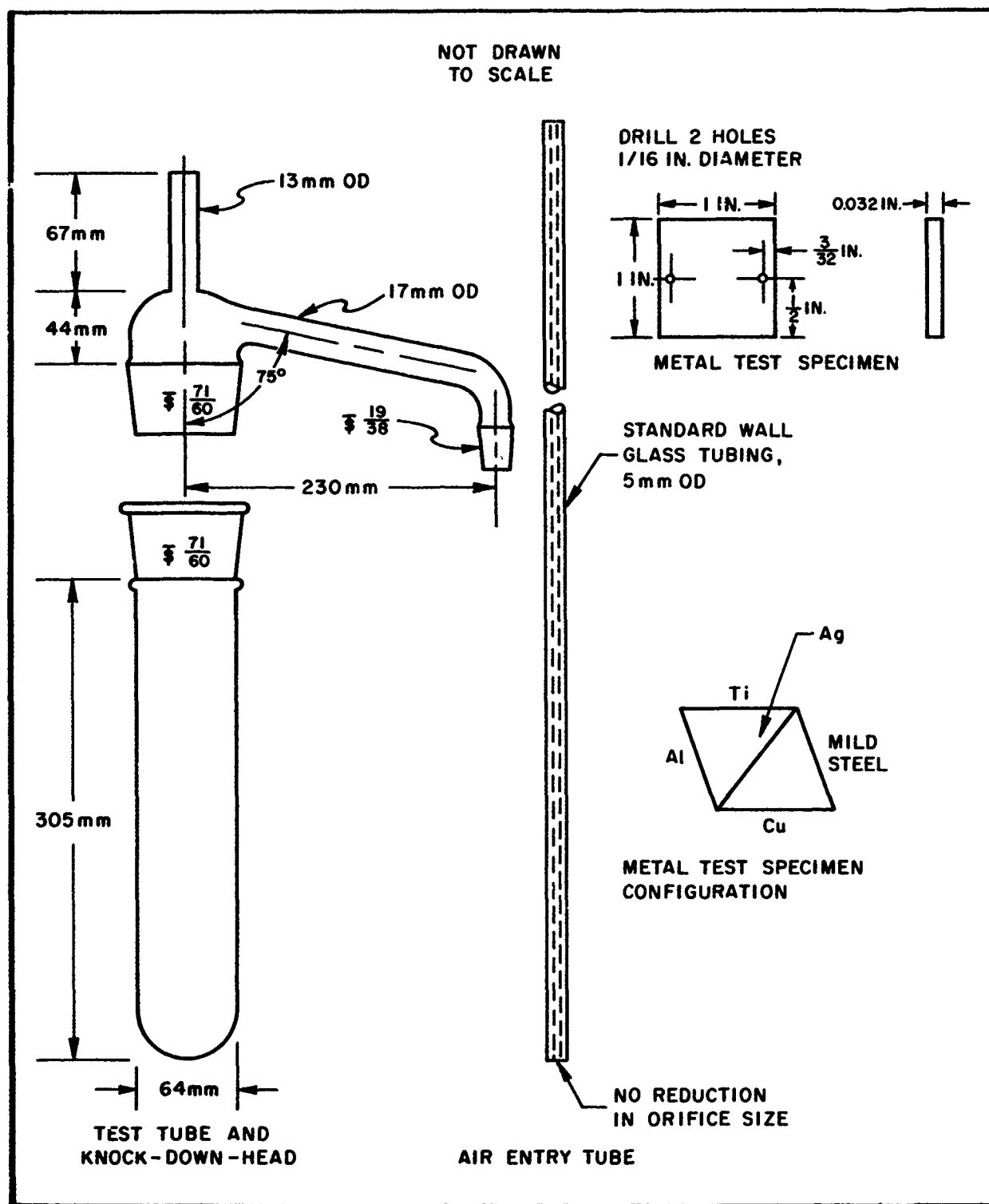


Figure 4. Celanese Bench Scale O-C Test Apparatus

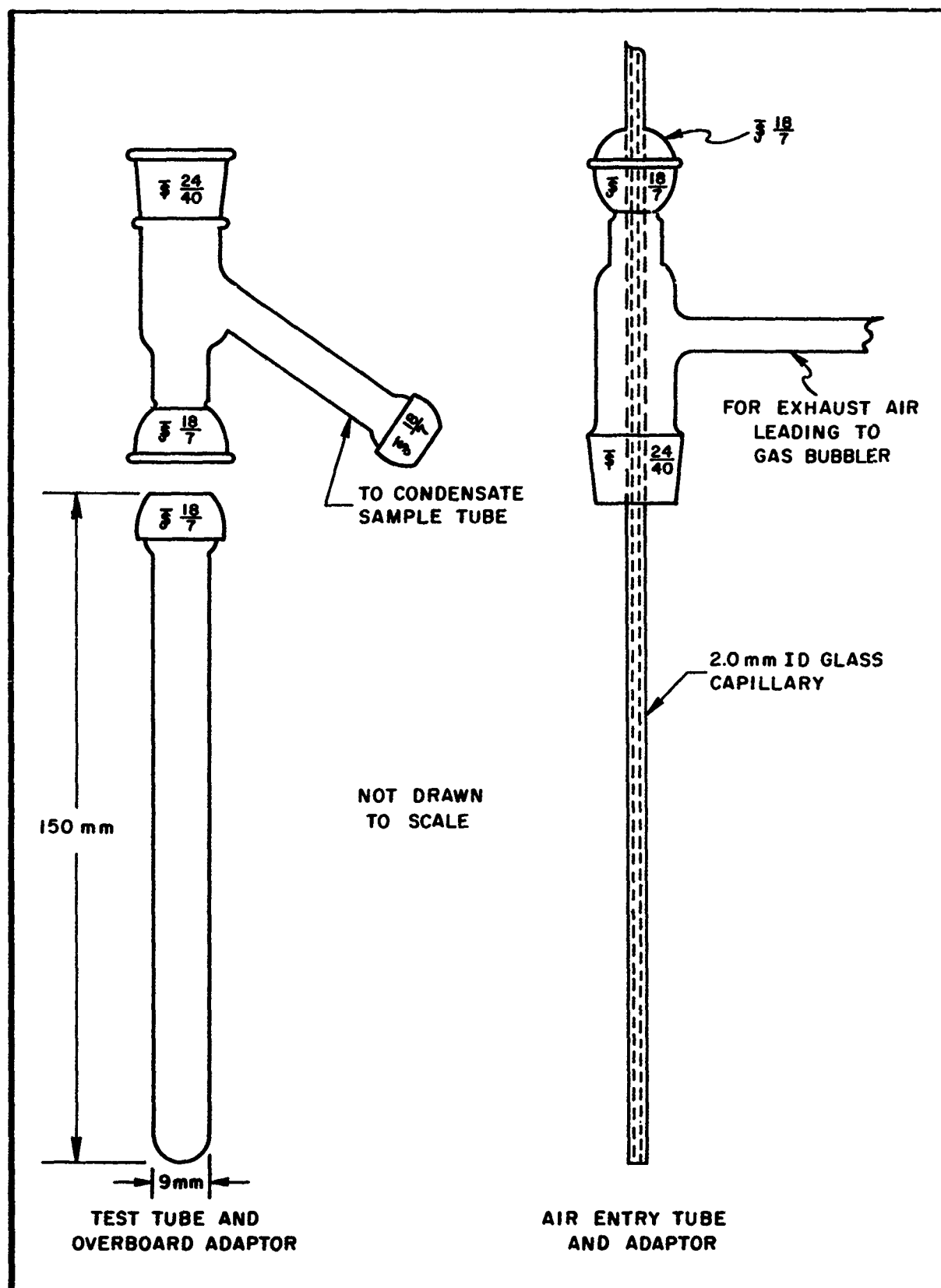


Figure 5. Wyandotte Miniature Oxidation Test Apparatus

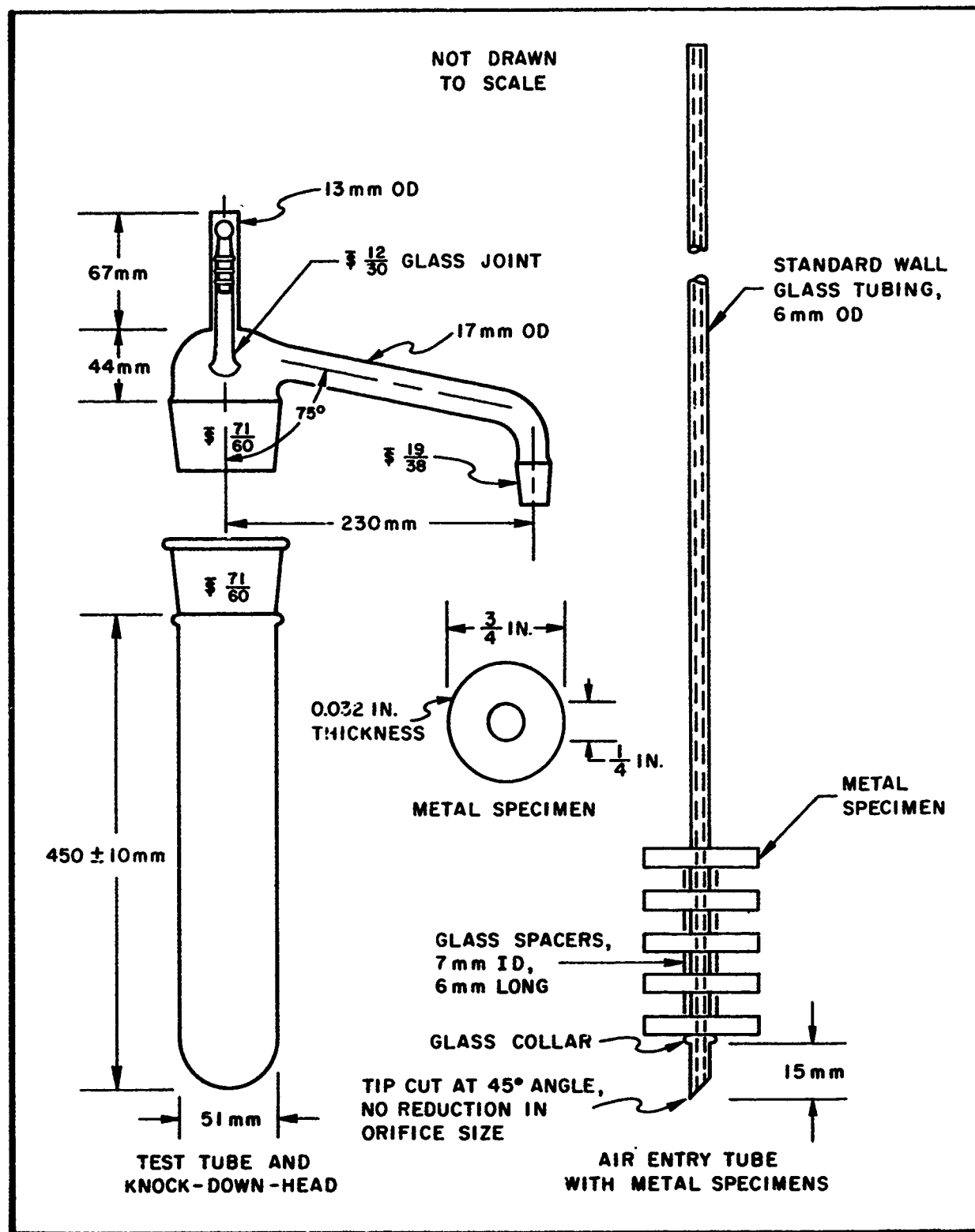


Figure 6. SwRI 500° F + Bench Scale O-C Test Apparatus

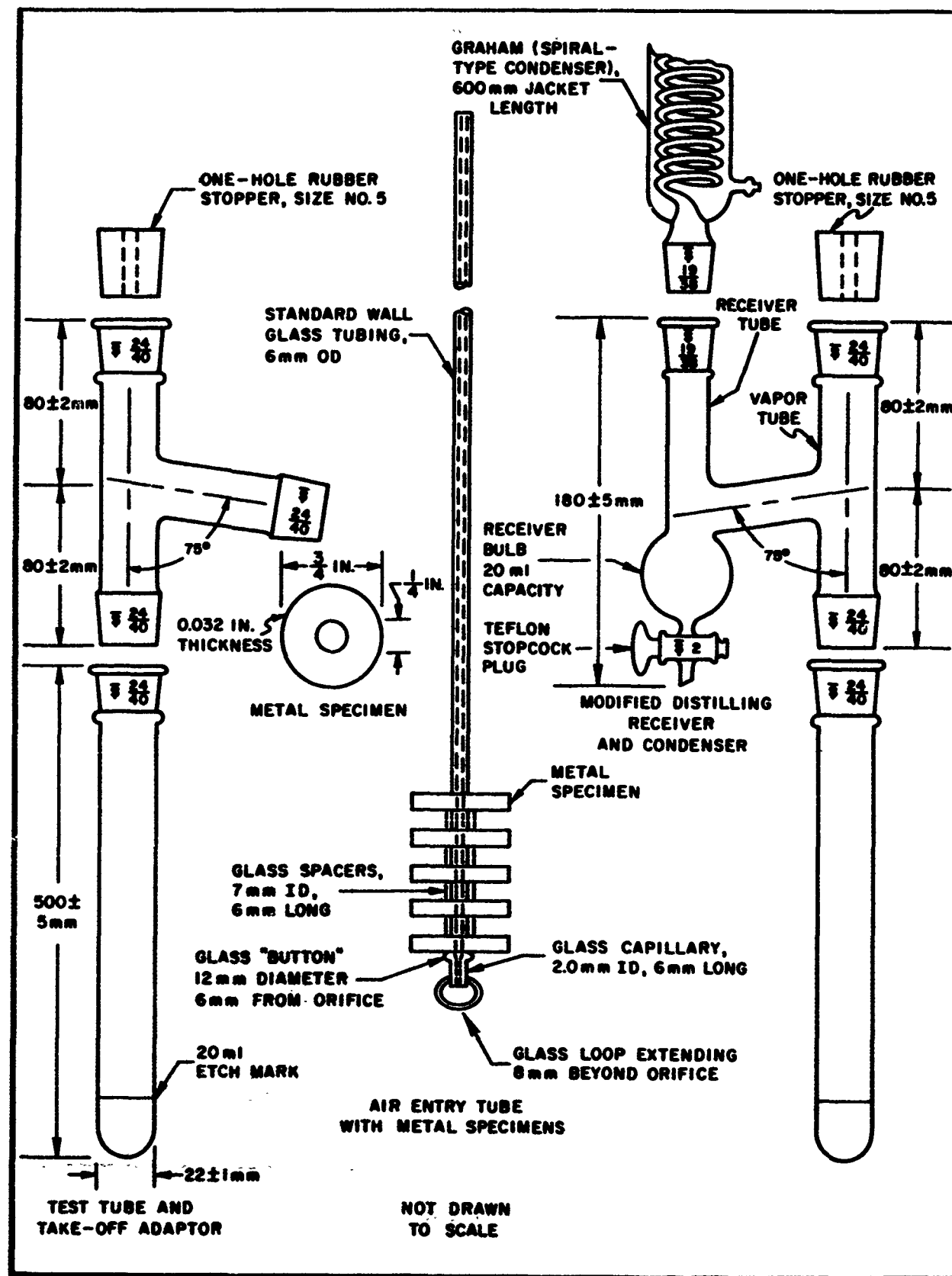


Figure 7. MANL Improved Micro O-C Test Apparatus

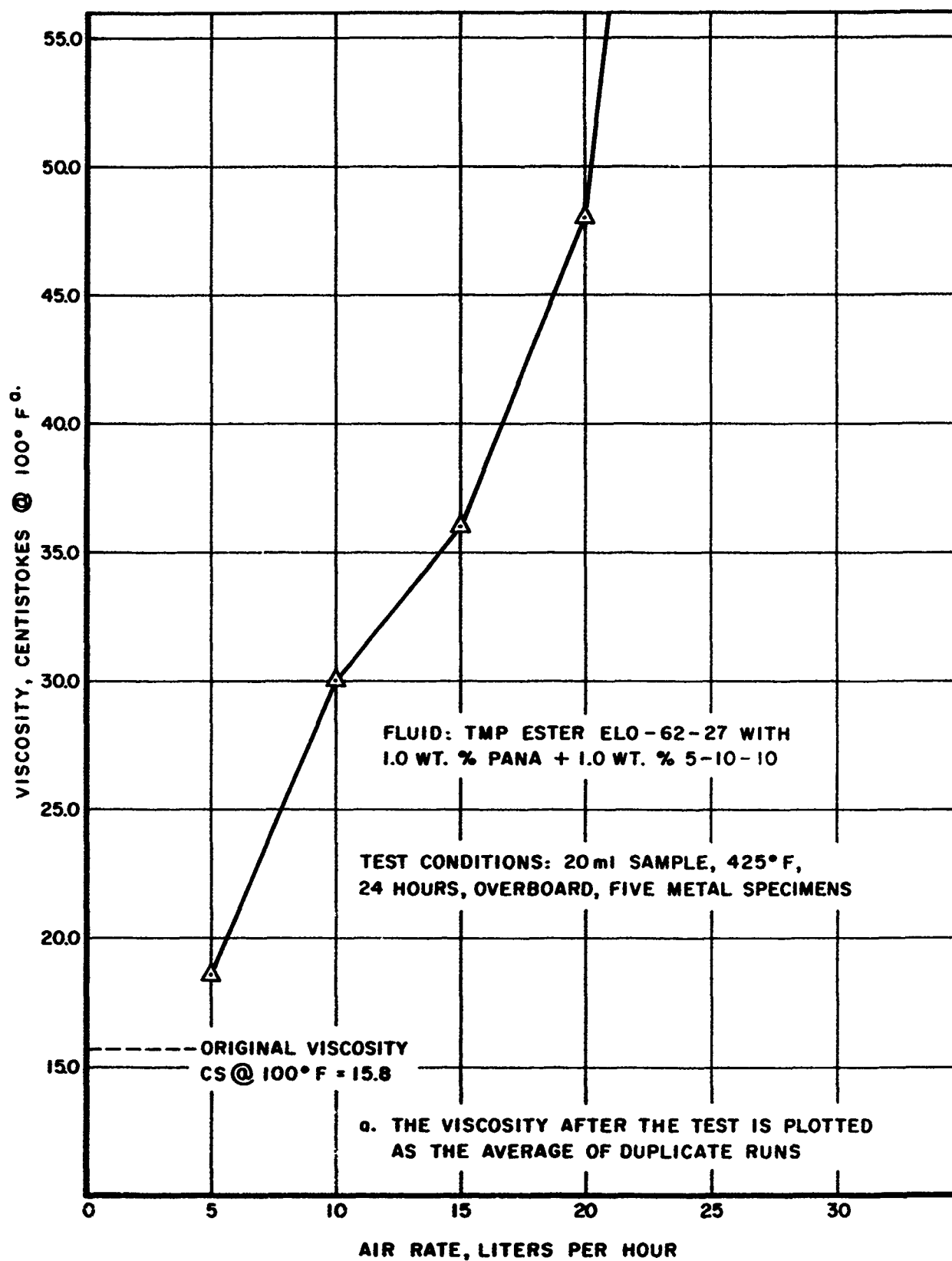


Figure 8. Effect of Air Flow Rate on the Viscosity of Formulated ELO-62-27 in the MANL Improved Micro O-C Test

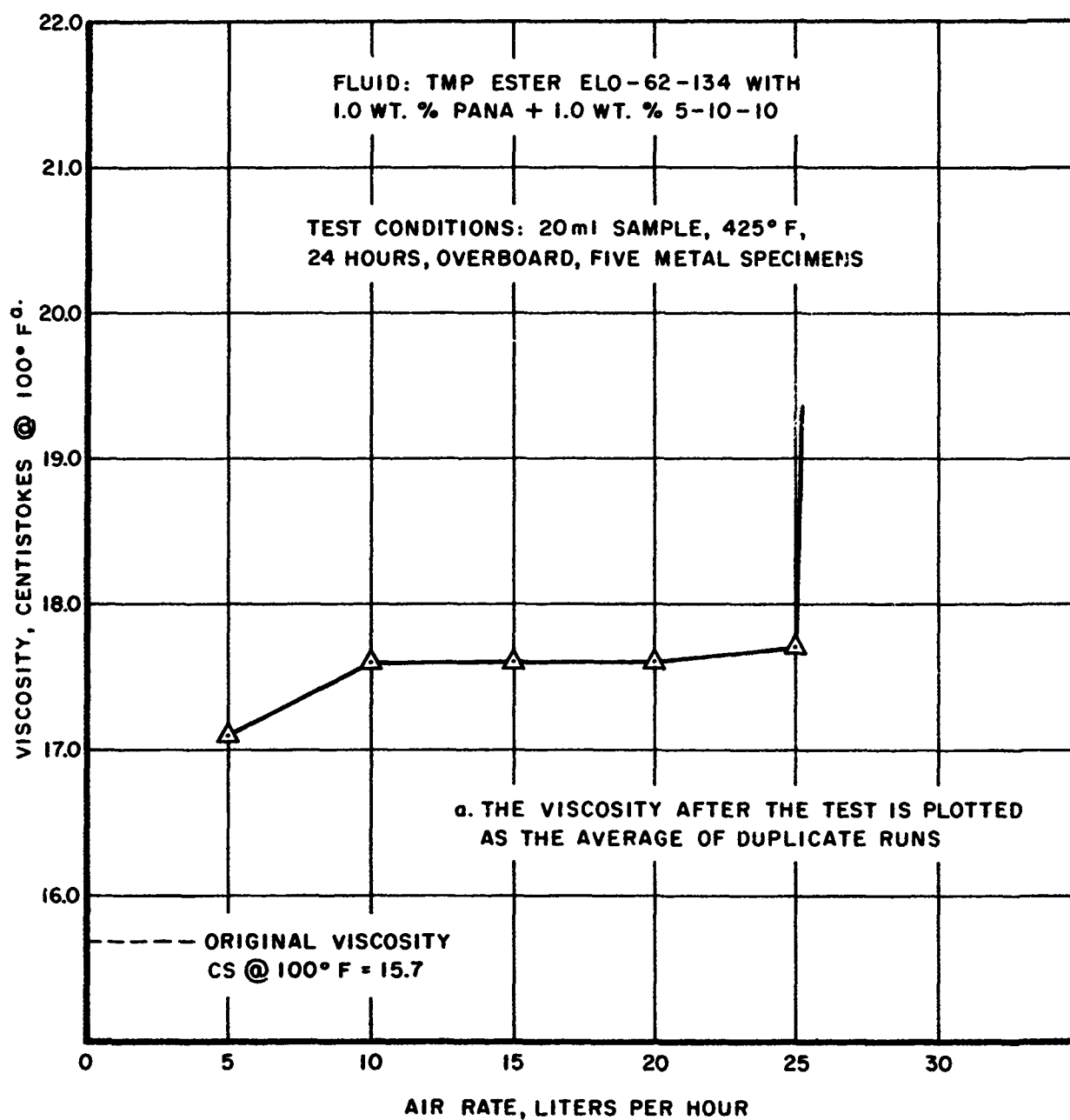


Figure 9. Effect of Air Flow Rate on the Viscosity of Formulated ELO-62-134 in the MANL Improved Micro O-C Test

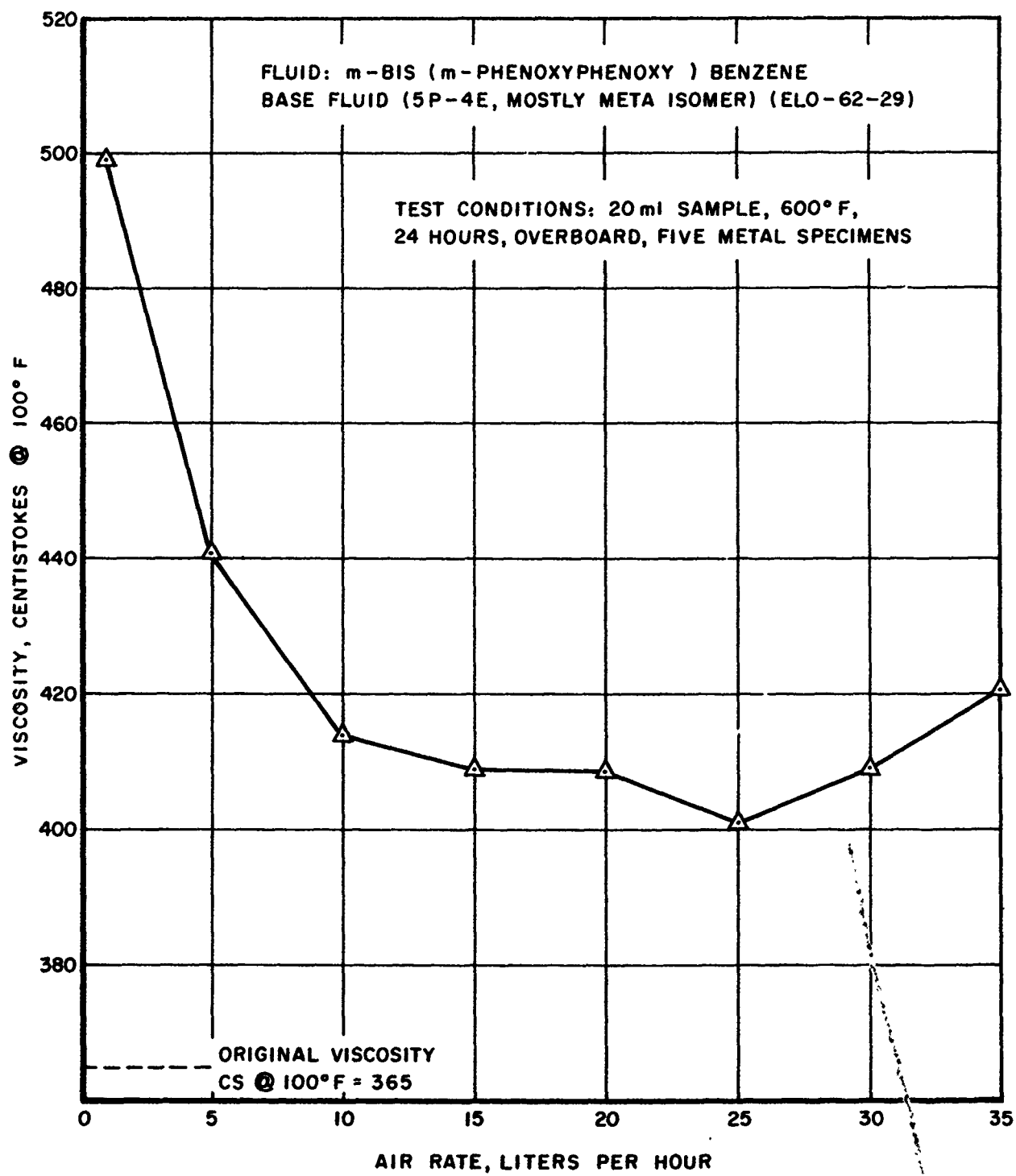


Figure 10. Effect of Air Flow Rate on the Viscosity of 5P-4E Polyphenylether Base Fluid in the MANL Improved Micro O-C Test

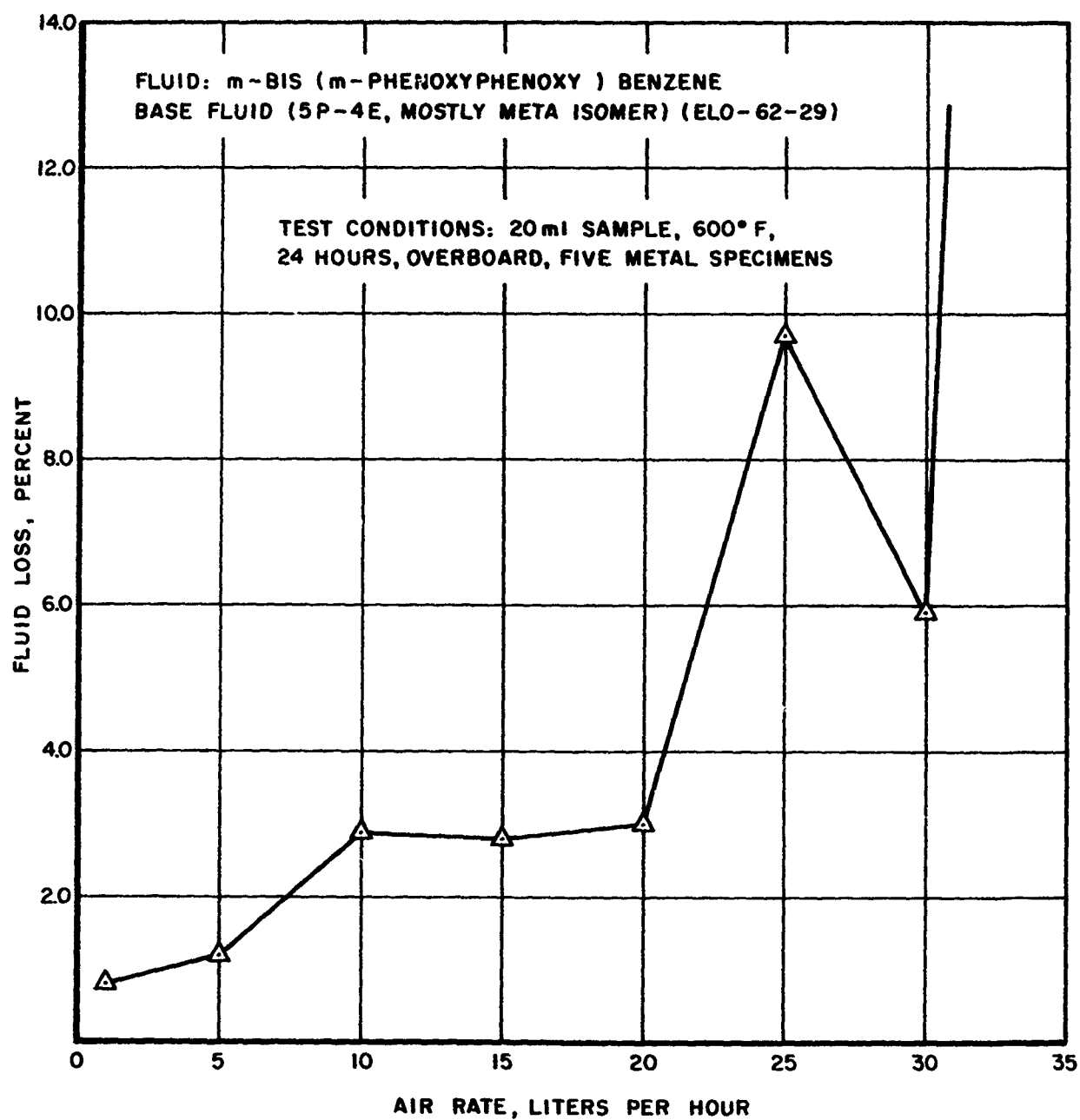


Figure 11. Effect of Air Flow Rate on the Fluid Loss of 5P-4E Polyphenylether Base Fluid in the MANL Improved Micro O-C Test

TABLE 1
Effect of MANL Improved Micro O-C Test^a on Standard Fluids

FLUID b.	Test Temp., °F.	Fluid Loss, %	Viscosity (cs) Increase @ 100°F %	Neut. Nr. Increase mg/KOH/g	Metal Wt. Change (mg/cm ²) and Appearance				REMARKS
					Titanium Alloy	Aluminum Alloy	M-10 Tool Steel	301 Stainless Steel	
SP-4E Polyphenylether Base Stock (ELO-62-29)	500	4.0	5.5	0.0	-0.02 L. T.	-0.04 N. T.	0.00 M. T.	-0.03 L. T.	Fluid slightly darkened. No insolubles formed.
SP-4E Polyphenylether Base Stock (ELO-62-29)	600	3.0	12.0	0.0	-0.02 L. T.	-0.01 N. T.	+0.02 D. T.	0.00 L. T.	Fluid darkened. No insolubles formed.
TMP Ester ELO-62-134 with 1.0 Wt. % PANA + 1.0 Wt. % S-10-10	425	5.0	12.4	0.2	0.00 L. T.	0.00 N. T.	0.00 M. T.	-0.02 L. T.	Fluid darkened. No insolubles formed.
TMP Ester ELO-62-27 with 1.0 Wt. % PANA + 1.0 Wt. % S-10-10	425	16.6	204	14.7	0.00 N. T.	+0.01 N. T.	0.00 L. T.	-0.23 L. T.	Fluid darkened. No insolubles formed.

a. Test conditions: 20 ml sample, 20 liters 1/hr. air flow rate, 24 hour duration, overboard.

b. The data given for each fluid is an average of closely agreeable duplicate tests.

N. T. = No tarnish or discoloration
L. T. = Light tarnish or discoloration
M. T. = Moderate tarnish or discoloration
D. T. = Dark tarnish or discoloration

TABLE 2
MANL Improved Micro O-C Test Versus SwRI Bench Scale O-C Test

FLUID	Test Method a.	Test Duration Hrs.	Test Temp., ° F	Fluid Loss, % b.	Viscosity (CS) @ 100° F			Neutralization Number, mg KOH/g		Metal Wt. Change (mg/cm ²) and Appearance j.				
					Before Test	After Test	% Change	Before Test	After Test	Titanium Alloy	Aluminum Alloy	M-10 Tool Steel	Silver	301 Stainless Steel
Resorcinyl dinonaphthoate formulation (ELO-62-50)	MANL	24 j.	425	7.8	20.5	22.0	7.3	<0.1	<0.1	+0.01 L. T.	+0.02 N. T.	+0.02 M. T.	+0.02 N. T.	+0.01 L. T.
	SwRI ^d	18	425	87	20.6	39.5	91.7	0.1	2.0	0.00	0.00	0.05	-0.02	0.00
Resorcinyl dinonaphthoate formulation (ELO-62-50)	MANL	24 j.	450	17.8	20.5	22.6	10.2	<0.1	0.1	0.00 L. T.	+0.01 L. T.	0.00 L. T.	+0.01 L. T.	+0.02 L. T.
	SwRI ^d	18	450	81	20.6	35.5	72.3	0.1	2.5	g.	g.	+0.04	-0.04	+0.04
Resorcinyl dinonaphthoate formulation (ELO-62-50)	MANL	24 j.	475	22.1	20.5	27.9	36.1	<0.1	0.5	+0.02 L. T.	+0.09 L. T.	g. M. T.	+0.06 L. T.	+0.06 L. T.
	SwRI ^d	18	475	59	20.6	26.2	27.1	0.1	1.3	+0.10	+0.13	+0.16	+0.13	+0.12
Resorcinyl dinonaphthoate formulation (ELO-62-50)	MANL	24 j.	500	34.7	20.5	1.	-	<0.1	28	+0.02 L. T.	+0.08 M. T.	+0.08 D. T.	+0.03 L. T.	+0.02 M. T.
	SwRI ^d	18	500	71	20.6	190	822	0.1	8.4	+0.12	+0.04	+0.22	+0.12	+0.24
Polyester formulation (ELO-62-39) n.	MANL	24 j.	450	11.8	41.3	48.0	16.2	<0.1	<0.1	0.00 L. T.	0.00 N. T.	-0.02 L. T.	-0.22 N. T.	+0.01 N. T.
	SwRI ^d	18 j.	450	7	41.8	46.5	11.2	0.1	0.1	-0.01	-0.01	-0.01	-0.21	+0.08
Polyester formulation (ELO-62-39) n.	MANL	24 j.	500	27.0	41.3	65.1	57.6	<0.1	<0.1	+0.16 L. T.	+0.01 N. T.	+0.04 M. T.	-0.02 L. T.	+0.03 L. T.
	SwRI ^d	18 j.	500	29	41.8	56.2	34.4	0.1	0.3	0.00	0.00	-0.32	-0.11	0.00
SP-4E Polyphenylether base fluid (ELO-62-23) f.	MANL	24 j.	600	3.0	365	408	12.0	<0.1	<0.1	-0.02 L. T.	-0.01 N. T.	+0.02 D. T.	-0.02 L. T.	0.00 L. T.
	SwRI ^e	24	600	60	362	478	32	<0.1	<0.1	h.	h.	h.	h.	h.
Trimethylolpropane tribenzoate (ELO-62-27) m.	MANL	24 j.	425	16.6	15.8	48.0	204	<0.1	14.7	0.00 N. T.	+0.01 N. T.	0.00 L. T.	-0.22 L. T.	0.00 N. T.
	SwRI ^d	18 k.	425	25	16.0	23.8	48.8	<0.1	4.7	-0.01	0.00	+0.01	-0.06	0.00

N. T. = No tarnish or discoloration
L. T. = Light tarnish or discoloration
M. T. = Moderate tarnish or discoloration
D. T. = Dark tarnish or discoloration

- In all MANL tests 20 liters/hr air was passed through a 20 milliliter sample (overboard).
- The percent fluid loss for all the SwRI tests was estimated. The data taken from References 6 and 9 gave fluid loss in grams and initial charge in milliliters.
- Mild steel was used in all the SwRI tests instead of tool steel.
- Test conditions: 350 milliliter sample, 196 liters/hr air flow rate, overboard.
- Test conditions: 250 milliliter sample, 130 liters/hr air flow rate, overboard.
- Designated as LEO-13 in SwRI reference data.
- Error in metal weight change suspected.
- Metal wt. change not recorded in SwRI reference data.
- The appearance of the metals after the test was not included in the SwRI reference data.
- Average of closely agreeable duplicate tests.
- Average of three tests.
- The fluid darkened badly and was only slightly mobile at room temperature.
- Different lots of the base stock were used at each laboratory, designated as 0-60-23 in SwRI reference data.
- Designated as MLO-62-1005 in SwRI reference data.

TABLE 3

Effect of Air Flow Rate on the Stability of Formulated ELO-62-27 in the
MANL Improved Micro O-C Test

Air Flow Rate, Liters/Hour	5	10	15	20	25
Viscosity at 100°F After Test, CS a.	17.3 20.0	31.1 28.8	24.5 47.6	49.6 46.4	296 305
Viscosity Increase at 100°F, %	9.5 26.6	96.8 82.3	55.1 201	214 194	1770 1830
Neutralization No. Increase, mg KOH/g b.	0.4 3.2	9.5 15.1	15.1 17.9	16.5 12.9	12.4 15.1

NOTE: The double values given in the table represent the results of duplicate tests.
Test Conditions: 20 ml sample, 425°F, 24 hour duration, 5 metal specimens, overboard.

a. Viscosity before the test was 15.8 centistokes

b. Neutralization number before the test was 0.2 mg KOH/g.

TABLE 4

Effect of Air Flow Rate on the Stability of Formulated ELO-62-134 in
the MANL Improved Micro O-C Test

Air Flow Rate, Liters/Hour	5	10	15	20	25	30
Viscosity at 100°F After Test, CS a.	17.1 17.1	17.7 17.4	17.8 17.4	17.5 17.8	17.7 17.7	885 155
Viscosity Increase at 100°F, %	8.9 8.9	12.7 10.8	13.4 10.8	11.5 13.4	12.7 12.7	5540 887
Neutralization No. Increase, mg KOH/g b.	0.0 0.2	0.3 0.4	0.4 0.2	0.3 0.0	0.0 0.0	7.2 11.2

NOTE: The double values given in the table represent the results of duplicate tests.
Test Conditions: 20 ml sample, 425°F, 24 hour duration, 5 metal specimens, overboard.

a. Viscosity before the test was 15.7 centistokes.

b. Neutralization number before the test was 0.4 mg KOH/g.

TABLE 5

Effect of Air Flow Rate on the Stability of 5P-4E Polyphenylether
Base Fluid in the MANL Improved Micro O-C Test

Air Flow Rate, Liters/Hour	1	5	10	15	20	25	30	35
Viscosity at 100°F After Test, CS a.	499	441	414 ^c	409	409 ^c	401 ^d	409 ^d	421
Viscosity Increase at 100°F, %	36.7	20.8	13.4	12.0	12.0	9.9	12.0	15.3
Neutralization No. Increase, mg KOH/g b.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fluid Loss, %	0.8	1.2	2.9 ^c	2.8	3.0 ^c	9.7 ^d	5.9 ^d	38.7

NOTE: The values given in the table represent the results of a single test unless otherwise indicated.

Test Conditions: 20 ml sample, 600°F, 24 hour duration. 5 metal specimens, over-board.

- a. Viscosity before the test was 365 centistokes.
- b. Neutralization number before the test was <0.1 mg KOH/g.
- c. The average value of duplicate tests
- d. The average value of three tests

TABLE 6
Improved Micro Oxidation Test^{a.} Versus Wyandotte Miniature Oxidation Test^{b.}

FLUID	Test Method c.	Fluid Loss, %	Viscosity (CS) @ 100° F			Appearance of Fluid After Test	IR Change h.
			Before Test	After Test	% Change		
Versilube F-50 Silicone (ELO-62-13)	MANL	8.3	47.7	245	414	Slightly Yellowed	-
	g. WYAND	6.5	47.8	153	220	No Change	No
DC-710 Silicone (ELO-64-17)	MANL	1.8	227	239	5.3	No Change	-
	WYAND	3.9	233	258	10.7	Slightly Darkened	No
5P-4E Polyphenylether (ELO-62-29)	MANL	0.8	365	380	4.1	Slightly Darkened	-
	g. WYAND	2.3	373	386	3.5	No Change	No
Diphenyl-di-n-dodecylsilane (ELO-62-14)	MANL	33.3	37.1	1690	4460	Darkened	-
	g. WYAND	13.6	37.4	736	1870	Darkened	Yes
Octadecyl tri-n-dodecylsilane (ELO-62-15)	MANL	30.9	34.8	1110	3090	Darkened	-
	WYAND.	44.5	35.6	d.	-	Blackened	Yes
Tris isooctylamine (ELO-62-19) e.	MANL	28.6	9.4	d.	-	Darkened Badly	-
	WYAND	54.1	9.4	d.	-	Blackened	Yes
Deep-dewaxed mineral oil formulation (ELO-62-18)	MANL	11.3	76.5	d.	-	Darkened Badly	-
	WYAND	22.6	76.9	d.	-	Blackened	Yes
Trimethylolpropane triheptanoate (ELO-62-27) f.	MANL	37.6	15.1	673	4360	Darkened Badly	-
	WYAND	61.3	15.5	d.	-	Blackened	Yes
2-Phenoxy-3-(5-nonyl)pyrazine (ELO-63-198)	MANL	10.0	19.7	25.9	31.5	Darkened Badly	-
	WYAND	10.3	21.4	28.1	31.3	Blackened	Slight

a. Test Conditions: 20 ml sample, 500° F, 20 liters/hour air flow rate, 6 hour duration, no metal specimens, overboard
b. Test Conditions: 2.0 ml sample, 500° F, 2.0 liters/hour air flow rate, 6 hour duration, no metal specimens, overboard
c. Only single tests were made unless otherwise indicated.
d. Fluid was too dark and viscous (tarred) for practical viscosity measurements.
e. Designated as MLO-60-126 in Wyandotte reference data.
f. Designated as MLO-60-50 in Wyandotte reference data.
g. Average results of duplicate tests.
h. IR change was not determined at MANL.

TABLE 7
Improved Micro O-C Test a. Versus Phoenix Micro O-C Test b.

FLUID	Test Method	Test Temp. °F	Fluid Loss, %	Viscosity (CS) @ 100°F			Neutralisation Number, mg KOH/g	Metal Wt. Change, mg/cm ²					REMARKS
				Before Test	After Test	% Change		Titanium Alloy	Aluminum Alloy	M-10 Tool Steel	Silver	301 Stainless Steel	
5P-4E Polypheylether base stock (ELO-62-26)	MANL	500	2.1	365	378	3.6	<0.1		No Metals Used				Fluid slightly darkened. No insoluble formation.
	PHOENIX	500	5.2	365	378	4.4	<0.1		No Metals Used				Fluid became medium amber. No insoluble formation.
5P-4E Polypheylether base stock (ELO-62-26)	MANL	500	4.1	365	385	5.5	<0.1	-0.02	-0.04	0.00	-0.03	-0.02	Fluid slightly darkened. No insoluble formation.
	PHOENIX	500	3.7	365	385	5.5	<0.1	-0.02	-0.04	0.00	-0.03	-0.02	Fluid became medium to dark amber. No insoluble formation.
5P-4E Polypheylether base stock (ELO-62-26)	MANL	500	3.5	360	377	4.7	<0.1	0.00	0.00	0.00	0.00	0.00	Fluid darkened. No insoluble formation.
	PHOENIX	500	4.3	360	377	4.7	<0.1	0.00	0.00	0.00	0.00	0.00	Fluid became dark amber. No insoluble formation.
5P-4E Polypheylether base stock (ELO-62-26)	MANL	600	2.4	365	410	12.3	<0.1	-0.02	-0.01	+0.01	-0.02	0.00	Fluid darkened. No insoluble formation.
	PHOENIX	600	3.6	365	408	11.8	<0.1	-0.02	-0.01	+0.02	-0.02	-0.01	Fluid became dark amber. No insoluble formation.
Resorcinyl diisocyanate formulation (ELO-62-50)	MANL	450	15.7	20.5	21.1	2.9	<0.1		No Metals Used				Fluid darkened. A negligible sludge formation.
	PHOENIX	450	16.7	20.5	21.1	2.9	<0.1		No Metals Used				Fluid became dark amber. No insoluble formation.
Resorcinyl diisocyanate formulation (ELO-62-50)	MANL	450	16.1	20.4	22.5	10.3	0.1	-0.01	0.00	-0.01	0.00	+0.02	Fluid darkened. A negligible sludge formation.
	PHOENIX	450	16.3	20.5	22.5	9.8	<0.1	-0.01	0.00	-0.01	+0.02	+0.02	Fluid became dark amber. No insoluble formation.
Resorcinyl diisocyanate formulation (ELO-62-50)	MANL	475	23.2	20.4	23.4	14.7	0.1	0.00	0.00	0.00	-0.04	0.00	Fluid darkened. No insoluble formation.
	PHOENIX	475	23.3	20.5	23.8	16.1	<0.1		No Metals Used				Fluid became dark amber. No insoluble formation.
Resorcinyl diisocyanate formulation (ELO-62-50)	MANL	475	16.6	20.4	25.2	23.5	0.1	0.00	+0.09	d	+0.06	+0.06	Fluid darkened. No insoluble formation.
	PHOENIX	475	20.4	20.5	30.4	48.3	<0.1	0.00	+0.09	d	+0.06	+0.06	Fluid became dark amber. No insoluble formation.
P-(p-t-Butylphenoxy) phenyl isocyanate base stock (ELO-62-93)	MANL	450	10.5	72.5	106	46.2	0.2		No Metals Used				Fluid slightly darkened. No insoluble formation.
	PHOENIX	450	13.8	72.1	101	40.1	0.2		No Metals Used				Fluid became a dark amber. No insoluble formation.
P-(p-t-Butylphenoxy) phenyl isocyanate base stock (ELO-62-93)	MANL	450	4.2	72.5	100	38.0	<0.1	+0.04	+0.08	0.00	+0.02	+0.06	Fluid darkened. No insoluble formation.
	PHOENIX	450	20.8	72.1	114	58.1	<0.1	-0.02	0.00	-0.02	-0.04	-0.04	Fluid became dark amber. No insoluble formation.

- a. Test Conditions: 20 ml sample, 20 liters/hour air flow rate, 24 hour duration, overboard
b. Test Conditions: 20 ml sample, 20 liters/hour air flow rate, 24 hour duration, overboard
c. Double values represent duplicate test results.
d. Mistake in weighing suspected.
e. The appearance of the metal specimens after the test was not included in the data. Since the same nomenclature was not used at the two laboratories a meaningful comparison could not be made.